Sym $N,N',N''$-Tri(4-tolyl)guanidine Derived Six-Membered $[C,N]$ Palladacycles: Synthesis, Reactivity Studies and Structural Aspects

2.1.1 ABSTRACT

The reaction of Pd(OC(O)CF$_3$)$_2$ and Pd(OC(O)Bu)$_2$ carried out separately with LH$_2$$_{4}$$_{4}$-tolyl in 1:1 ratio in toluene at 70 °C for 6 h afforded six-membered $[C,N]$ palladacycles $\text{[Pd}\{\kappa^2(C,N)-C_6H_3Me-5(NHC(NHAr)(=NAr))-2\}(\mu-OC(O)R)]_2$ (Ar = 4-MeC$_6$H$_4$, R = CF$_3$ (I); Bu (II)) in 91 and 92 % yields, respectively. Palladacycle I was subjected to a metathetical reaction with LiBr in aq. ethanol at 80 °C for 3 h to afford bromo bridged six-membered $[C,N]$ palladacycle $\text{[Pd}\{\kappa^2(C,N)-C_6H_3Me-5(NHC(NHAr)(=NAr))-2\}(\mu-Br)]_2$ (Ar = 4-MeC$_6$H$_4$) (III) in 95% yield. Palladacycles I and III were subjected to a bridge splitting reaction with Lewis bases (L’s) in CH$_2$Cl$_2$ separately at ambient temperature to afford monomeric six-membered $[C,N]$ palladacycles $\text{[Pd}\{\kappa^2(C,N)-C_6H_3Me-5(NHC(NHAr)(=NAr))-2\}(OC(O)CF_3)(L)]$ (Ar = 4-MeC$_6$H$_4$; L = 2,6-Me$_2$C$_5$H$_3$N (IV), 1,3,5-triaza-7-phosphaadamantane (PTA) (V), $\text{[Pd}\{\kappa^2(C,N)-C_6H_3Me-5(NHC(NHAr)(=NAr))-2\}Br(L)](\text{Ar} = 4$-MeC$_6$H$_4$; L = 2,6-Me$_2$C$_5$H$_3$N (VI), PTA (VII)) in 93–96% yield. Further, palladacycle III was treated with Na(acac) (acac: acetylacetonate) in CH$_2$Cl$_2$ at ambient temperature to afford aspirocyclic six-membered $[C,N]$ palladacycle $\text{[Pd}\{\kappa^2(C,N)-C_6H_3Me-5(NHC(NHAr)(=NAr))-2\}(\kappa^2-O,O'-acac)](\text{Ar} = 4$-MeC$_6$H$_4$; VIII) in 93% yield. The molecular structures of I–VI were determined by single crystal X-ray diffraction data. Palladacycles I and II exist as a dimer in transoid in-in conformation in the solid-state. Palladacycle III was shown to possess a transoid arrangement with two halves of the molecule related by a centre of symmetry and the $\text{[Pd}(\mu-Br)\text{Pd}]^{2+}$ unit was shown to be planar. Palladacycles IV–VI are monomeric with the Lewis base placed trans to the imine nitrogen around the palladium atom due to antisymbiosis.

2.1.2 INTRODUCTION

The imine derived six-membered $[C,N]$ palladacycles are one of the interesting classes of palladacycles due their relevance as pre-catalysts in C–C and C–heteroatom bond forming reactions, their intriguing structural and reactivity pattern including
regioselective aspects of C–H activation process,\textsuperscript{5–11} and as scaffolds that exhibit an interesting photo physical properties.\textsuperscript{12,13} Further, the six-membered “[C,N]Pd” skeleton is often encountered as reactive intermediate in palladium mediated organic transformations.\textsuperscript{14,15}

We have recently reported the synthesis, reactivity studies, structural aspects, and solution dynamics of (ArNH)\textsubscript{2}C=NAr (Ar = 2-(MeO)C\textsubscript{6}H\textsubscript{4}; LH\textsubscript{2}\textsuperscript{2-anisyl}) derived six-membered and ring contracted five-membered [C,N] palladacycles.\textsuperscript{16} We want to address how the sterically less hindered and more symmetrical aryl moiety in (ArNH)\textsubscript{2}C=NAr (Ar = 4-MeC\textsubscript{6}H\textsubscript{4} (LH\textsubscript{2}\textsuperscript{4-tolyl})) than those present in LH\textsubscript{2}\textsuperscript{2-anisyl} and their conformational difference (anti-anti versus syn-anti αββ\textsuperscript{17}) influences the solid state structures and solution behaviour of LH\textsubscript{2}\textsuperscript{4-tolyl} derived [C,N] palladacycles. Towards these goals, we describe herein the synthesis, structural aspects and solution behaviour of LH\textsubscript{2}\textsuperscript{4-tolyl} derived dimeric [C,N] palladacycles I–III, monomeric [C,N] palladacycles IV–VII, and spirocyclic [C,N] palladacycle, VIII as illustrated in Chart 2.1.1.

2.1.3 RESULTS AND DISCUSSION

2.1.3.1 Cyclopalladation Reactions

2.1.3.2 Carboxylato Bridged Dimeric [C,N] Palladacycles (I and II)

Cyclopalladation reaction usually occurs through a C–H activation process.\textsuperscript{18} The reaction of Pd(OC(O)CF\textsubscript{3})\textsubscript{2} and Pd(OC(O)^\textsuperscript{t}Bu)\textsubscript{2} carried out separately with sym N,N',N''-tri(4-tolyl)guanidine (LH\textsubscript{2}\textsuperscript{4-tolyl}) in 1:1 ratio in toluene at 70 °C for 6 h afforded [C,N] palladacycles [Pd(κ\textsuperscript{2}(C,N)-C\textsubscript{6}H\textsubscript{3}Me-5(NHC(NHAr)(=NAr))-2)(µ-OC(O)R)]\textsubscript{2} (Ar = 4-MeC\textsubscript{6}H\textsubscript{4}, R = CF\textsubscript{3} (I); ^\textsuperscript{t}Bu (II)) as pale yellow-green crystals (I) and pale-yellow crystals (II) in 91 and 92% yield, respectively as shown in Scheme 2.1.1.

2.1.3.3 Solid State Structural Aspects

The molecular structures of I and II are depicted in Figure 2.1.1. Selected bond distances and bond angles are listed in Tables 2.1.1 and 2.1.2, respectively. Palladacycles I and II exist as a dimer wherein two palladium atoms are bridged by a pair of syn-syn bidentate bridging trifluoroacetato and, pivalato moieties, respectively. Palladacyle I revealed a pseudo $C_2$ symmetry whereas palladacyle II displayed a
crystallographic $C_2$ symmetry that passes vertically across the centre of the Pd···Pd vector to afford transoid in–in conformation.

Chapter 2: Results and Discussion

Chart 2.1.1

![Chart 2.1.1](image)

The palladium atom is surrounded by two oxygen atoms of the carboxylate moiety, an imine nitrogen and aryl carbon and thus displayed a distorted square planar geometry. The dihedral angle between two mean planes defined by N–Pd–C and O–Pd–O units in I (5.63 (22)$^\circ$ and 2.92(6)$^\circ$) and II (4.84 (6)$^\circ$) clearly reflects the distortion of the square planar geometry. The six-membered "[C,N]Pd" rings in I and II exhibited a pseudo boat conformation. The Pd–N distance in I (2.003(4) and 2.019(4) Å) and II (2.014(2) Å) are slightly shorter than the predicted value of 2.07 Å (based on $r$(Pd(II)) = 1.39 Å and $r$(N) = 0.68 Å)$^{19}$ indicating the presence of a weak Pd–N multiple bonding. The Pd–N distances in I and II are somewhat comparable.
with those reported for 19 and 20, (2.000(2)–2.017(2) Å)\(^{16}\) and \(N,N’\)-diphenylbenzamidine derived \([C,N]\) palladacycle (2.014(2) Å).\(^{20}\) The Pd–C distance in I (1.956(5) and 1.946(5) Å) and II (1.959(3) Å) are somewhat comparable with those reported for 19 and 20 (1.956(4)–1.967(8) Å and 1.959(3) Å)\(^{16}\) and \(N,N’\)-diphenylbenzamidine derived \([C,N]\) palladacycle (1.960(3) Å),\(^{20}\) but shorter than the predicted value of 2.07 Å (based upon \(r(C) = 0.68\) Å and \(r(Pd(II)) = 1.39\) Å)\(^{19}\)

**Scheme 2.1.1**

![Scheme 2.1.1](image)

**Table 2.1.1 Selected Bond Distances (Å) and Bond Angles (deg.) for Palladacycle I**

<table>
<thead>
<tr>
<th>Bond Distances/ Bond Angles</th>
<th>I</th>
<th>II</th>
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<tr>
<td>Pd(1)-C(21)</td>
<td>1.956(5)</td>
<td>1.956(5)</td>
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<td>2.003(4)</td>
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<td>Pd(1)-O(3)</td>
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<td>2.003(3)</td>
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<td>Pd(1)-O(1)</td>
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<td>2.168(3)</td>
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<td>1.946(5)</td>
<td>1.946(5)</td>
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<td>2.019(4)</td>
<td>2.019(4)</td>
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<td>Pd(2)-O(2)</td>
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<td>2.110(4)</td>
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<tr>
<td>N(1)-C(12)</td>
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<td>1.310(6)</td>
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<td>N(2)-C(12)</td>
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<td>N(3)-C(20)</td>
<td>1.403(6)</td>
<td>1.403(6)</td>
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<td>N(4)-C(34)</td>
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<td>N(5)-C(34)</td>
<td>1.379(6)</td>
<td>1.379(6)</td>
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<td>N(6)-C(34)</td>
<td>1.345(6)</td>
<td>1.345(6)</td>
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<tr>
<td>Pd(1)--Pd(2)</td>
<td>3.0052(5)</td>
<td>3.0052(5)</td>
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</tbody>
</table>

**Notes:**
- For Palladacycle I, the values are given for the selected bond distances and angles.
- The bond distances and angles are measured in Angstroms (Å) and degrees (deg.), respectively.
- The values in parentheses indicate the uncertainty in the last digit of the measured value.
Table 2.1.2 Selected Bond Distances (Å) and Bond Angles (deg.) for Palladacycle II

<table>
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<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (deg.)</th>
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<tr>
<td>Pd(1)-O(1)</td>
<td>2.137(2)</td>
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<td>Pd(1)-O(2)</td>
<td>2.045(2)</td>
<td>93.1(1)</td>
</tr>
<tr>
<td>Pd(1)-N(1)</td>
<td>2.014(2)</td>
<td>175.0(1)</td>
</tr>
<tr>
<td>Pd(1)-C(10)</td>
<td>1.959(3)</td>
<td>91.1(1)</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.296(4)</td>
<td>122.4(2)</td>
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<tr>
<td>N(2)-C(1)</td>
<td>1.357(4)</td>
<td>122.7(3)</td>
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<tr>
<td>N(3)-C(1)</td>
<td>1.366(4)</td>
<td>127.1(3)</td>
</tr>
<tr>
<td>N(2)-C(9)</td>
<td>1.403(4)</td>
<td>121.9(3)</td>
</tr>
<tr>
<td>Pd(1)--Pd(1)</td>
<td>2.9215(9)</td>
<td></td>
</tr>
<tr>
<td>N(1)-C(1)-N(2)</td>
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<td></td>
</tr>
<tr>
<td>N(2)-C(1)-N(3)</td>
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</tr>
</tbody>
</table>

indicating some multiple-bond character in the Pd–C(aryl) linkage.\(^{21}\) The Pd–O distance in I (2.168(5) and 2.169(4) Å) and II (2.137(2) Å)\(^{21}\) trans to the aryl carbon are longer than those that are trans to the imine nitrogen I (2.090(3), 2.110(4) Å) and II (2.045(2) Å) due to higher trans influence of the aryl carbon than that of the imine nitrogen.\(^{22}\) The Pd--Pd non bonded distance in I (3.0052(5) Å) and II (2.9215(9) Å) are shorter than the sum of the Van der Waals radius of two palladium (3.26 Å),\(^{16,17}\) but longer than the sum of covalent radii (2.78 Å)\(^{11}\) of two palladium and hence the Pd--Pd interaction is considered as weak. The aforementioned Pd--Pd non bonded distances are somewhat comparable with that reported for I (3.005(2) Å) and II (3.013(4) Å).\(^{16}\)

The structure and bonding of the CN\(_3\) core in I–II can be understood from the values of Δ\(_{CN}\), and Δ\(_{CN'}\) defined in Figure 2.1.2. The Δ\(_{CN}\) value is the difference in the distance between the endocyclic C–N single bond and the endocyclic C=N double bond while Δ\(_{CN'}\) value is the difference in the distance between the exocyclic C–N single bond and the endocyclic C=N double bond and these values are used as a measure of the delocalization of π-electron density across the –N–C=N–amidine component of the guanidine moiety.\(^{25}\) The Δ\(_{CN}\) value 0.050(8) Å for the CN\(_3\) unit around Pd1 is comparable with Δ\(_{CN'}\) value 0.054(8) Å but the Δ\(_{CN}\) value 0.040(8) Å for the CN\(_3\) unit around Pd2 is smaller than the Δ\(_{CN'}\) value 0.074(8) Å in palladacycle I. The Δ\(_{CN}\): 0.061(6) Å and Δ\(_{CN'}\): 0.070(6) Å values around Pd1 in II are comparable within the experimental uncertainties. The smaller Δ\(_{CN}\) value compared with Δ\(_{CN'}\) around Pd2 in I may be ascribed to a better alignment of the lone pair on
Figure 2.1.1 The ORTEP representation of I (left) and II (right) at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
**Chapter 2: Results and Discussion**

**Figure 2.1.2** Definition of $\Delta_{CN}$ and $\Delta_{CN}'$ used to describe the bonding within the CN3 unit of the guanidine moiety of I and II.

endocyclic amino nitrogen with the C=N$\pi^*$ orbital than that on exocyclic amino nitrogen for n–π conjugation. Further, $\Delta_{CN}$ and $\Delta_{CN}'$ value around Pd1 in I are considerably smaller than that observed for LH$_2$4-tolyl ($\Delta_{CN} = 0.077(4)$ and $\Delta_{CN}' = 0.106(4)$ Å).$^{17}$ The amino nitrogens in I and II are planar.

### 2.1.3.4 Spectroscopic Data

The IR spectrum of I and II revealed a band at 3414 and 3387 cm$^{-1}$, respectively assignable to two distinct NH moieties. Palladacycles I and II revealed a band at 1633 and 1604 cm$^{-1}$, respectively assignable to the C=N moiety. The $\nu$(C=N) value of I and II is smaller than that reported for LH$_2$4-tolyl ($\nu$(C=N): 1641 cm$^{-1}$).$^{17}$ The $\Delta\nu = \nu$(CN)$_{\text{complex}} - \nu$(CN)$_{\text{guanidine}}$ for I and II are $-8$ and $-37$ cm$^{-1}$, respectively and these values indicate coordination of the guanidine moiety to the palladium atom through an imine nitrogen. Palladacycles I and II also revealed two signature bands at 1685 and 1512 cm$^{-1}$ (I) and 1628 and 1500 cm$^{-1}$ (II) assignable to $\nu_a$(OCO) and $\nu_s$(OCO) for the carboxylate moieties. The $\Delta\nu = \nu_a$(OCO) – $\nu_s$(OCO) = 173 and 128 cm$^{-1}$ values observed for I and II, respectively indicate syn-syn bidentate bridging carboxylate coordination mode.$^{26}$ Additionally, palladacyle I revealed two intense bands at 1206 and 1147 cm$^{-1}$ assignable to the C–F stretch of the CF$_3$ unit.$^{27}$

The $^1$H NMR spectrum of I revealed three singlets at $\delta_H$ 2.22, 2.37 and 2.42 ppm assignable to CH$_3$ protons of the guanidine. The $^{13}$C NMR spectrum of I revealed three
signals at $\delta_C$ 20.78, 20.90 and 20.94 ppm assignable to CH$_3$ carbon of the guanidine. In addition, two quartets were observed at $\delta_C$ 115.16 ($J_{CF} = 287.9$ Hz) and 163.54 ($J_{CF} = 37.5$ Hz) ppm, assignable to CF$_3$ and OCO carbon, respectively. The $^{19}$F NMR spectrum of I revealed a singlet at $\delta_F$ –75.0 ppm. The $\delta_F$ value of I is comparable with that reported for structurally related TFA bridged six-membered [C,N] palladacycle, 20 ($\delta_F$ –74.33, –74.39, –74.56 and –74.62 ppm). $^{16}$

The $^1$H NMR spectrum of II revealed a singlet at $\delta_H$ 0.78 ppm assignable to C(CH$_3$)$_3$protons. Further, three singlets were observed at $\delta_H$ 2.18, 2.37 and 2.38 ppm assignable to CH$_3$ protons of the guanidine. The $^{13}$C NMR spectrum of II revealed two peaks at $\delta_C$ 20.9 (br) and 21.1 assignable to three distinct CH$_3$ carbon nuclei. Two peaks were observed at $\delta_C$ 28.0 and 39.6 ppm assignable (C(CH$_3$)$_3$) and (C(CH$_3$)$_3$) carbons, respectively. Additionally, one characteristic peak was observed at $\delta_C$ 185.2 ppm assignable to (O=C(O)) carbon. It is to be noted that II exists as a transoid in-in conformation in the solid state. In solution, it is presumed that II exists as a mixture of transoid in-in, transoid in-out, transoid out-out isomers in solution, and the rate of interconversion among these isomers could be faster than NMR time scale. As a result, II revealed the averaged signals of all three isomers and hence the spectrum apparently indicated the presence of only one isomer in solution as revealed by both $^1$H and $^{13}$C NMR data (see Scheme 1.3.2 in Chapter 1).

2.1.3.5 Metathetical Reaction

Palladacycle I was subjected to a metathetical reaction with LiBr in aq. ethanol at 80 °C to affordbromo bridged [C,N] palladacycle [Pd{$^4_2(C,N)$-C$_6$H$_3$Me-5(NHC(NHAr)(=NAr))-2}{(\mu-Br)}$_2$ (Ar=4-MeC$_6$H$_4$) (III) as yellow crystals in 95% yield as illustrated in Scheme 2.1.2.

2.1.3.6 Solid-State Structural Aspects

Suitable crystals of III were grown from chloroform/toluene mixture at ambient temperature. Palladacycle III crystallized in triclinic $\overline{P}$I space group. The molecular structure of III is depicted in Figure 2.1.3. Selected bond distances and bond angles are
listed in Table 2.1.3. The palladium atom in III is surrounded by two bromide, imine nitrogen and aryl carbon and thus revealed a slightly distorted square planar geometry. The dihedral angle between two mean planes defined by Br1–Pd1–Br1 and C10–Pd1–N1 units is 5.27(11)°. Palladacycle III exists as a dimer in transoid conformation.

**Scheme 2.1.2**

Two halves of the molecules are related by inversion symmetry. The [Pd(μ-Br)₂Pd]²⁺ unit revealed a planar rhomboid conformation (Pd(1)–Br(1)–Pd(1): 95.43(13)°; Br(1)–Pd(1)–Br(1): 84.57(1)°) as previously noted for 27, 29, 31, and 33 (see Chapter 1). The six-membered "[C,N]Pd" ring revealed a pseudo boat conformation. The Pd1–Br1 bond trans to the metalted carbon is longer than that trans to the imine nitrogen (2.5931(4); 2.4492(4) Å) as a result of greater trans influence of the aryl carbon. The Pd–C distance, 1.983(3) Å in III is somewhat comparable with that reported for the structurally related six-membered [C,N] palladacycles 27 (Pd–C: 1.985(4) Å) but shorter than that observed for 29 (Pd–C = 2.021(7) Å) perhaps owing to π-back bonding component present in the III. Δ_CN 0.050(6) Å is comparable with the Δ_CN': 0.053(6) Å within the experimental uncertainties. The amino nitrogens are planar. Palladacycle III is stabilized two pairs of intermolecular C–H···Br hydrogen bonding. In addition the reference molecule also forms a pair of intermolecular C–H···Cl hydrogen bonding with CHCl₃ as illustrated in Figure S2.1.1.
Figure 2.1.3 The ORTEP representation of III at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Table 2.1.3 Selected Bond Distances (Å) and Bond Angles (deg.) for Palladacycle III.

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<th>III</th>
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<td>C(10)-Pd(1)-N(1)</td>
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<td>C(1)-N(2)-C(9)</td>
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<td>Pd(1)-N(1)</td>
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<td>C(1)-N(3)-C(16)</td>
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<tr>
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<td>C(10)-N(1)-Pd(1)</td>
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</table>

2.1.3.7 Spectroscopic Data

The IR spectrum of III revealed two bands at 3404 and 1625 cm⁻¹ assignable to NH and C=N stretches, respectively. The ESI–MS⁺ spectrum of III revealed peaks at m/z (intensity %): 516.8987 (94) and 514.9304 (65) assignable to [(C,N)PdBr + 2H]⁺ and [(C,N)PdBr]⁺ fragments, respectively. The ¹H NMR spectrum of III revealed three singlets at δH 2.22, 2.30 and 2.34 ppm assignable to CH₃ protons of the guanidine. The ¹³C NMR spectrum of III revealed three peaks at δC 20.9, 21.1 and 21.2 ppm assignable to CH₃ carbon.

2.1.3.8 Reactivity Studies

Palladacycle I was subjected to a bridge splitting reaction with 2,6-lutidine and PTA separately in CH₂Cl₂ at ambient temperature to afford monomeric six-membered [C,N] palladacycles [Pd{κ²(C,N)-C₆H₅Me-5(NHC(NHAr)(=NAr))=O}(OC(O)CF₃)(L)](Ar= 4-MeC₆H₄; L = 2,6-Me₂C₅H₃N (IV), 1,3,5-triaza-7-phosphaadamantane (PTA) (V) in 96 and 94% yield, respectively. Similarly, palladacycle III was subjected to bridge splitting reaction with 2,6-lutidine and PTA separately in CH₂Cl₂ at ambient temperature to afford [Pd{κ²(C,N)-C₆H₅Me-5(NHC(NHAr)(=NAr))=O}(OC(O)CF₃)(L)](Ar= 4-MeC₆H₄; L = 2,6-Me₂C₅H₃N (VI), PTA (VII) in 97 and 96% yield, respectively as illustrated in Scheme 2.1.3, path a. Further, palladacycle III was treated with Na(acac) (acac = acetylacetonate) in CH₂Cl₂ at ambient temperature to afford spirocyclic [C,N] palladacycle [Pd{κ²(C,N)-C₆H₅Me-5(NHC(NHAr)(=NAr))=O}(κ²-O,O′-acac)](Ar = 4-MeC₆H₄; VIII) in 97% yield (see Scheme 2.1.3, path b).
2.1.3.9 Solid State Structural Aspects

Palladacycles IV–VI were crystallized from CH₂Cl₂/MeOH mixture at ambient temperature. In palladacycles IV and VI, two molecules crystallized in an asymmetric unit in monoclinic C2/c and triclinic PĪ space groups, respectively. Palladacycle V crystallized in monoclinic C2/c space group. The molecular structures of IV, V and VI are depicted in Figures 2.1.4–2.1.6, respectively. Selected bond distances and bond angles of IV, V and VI are listed in Table 2.1.4–2.1.6, respectively. The palladium atom in IV–VI is surrounded by imine nitrogen, aryl carbon, the nitrogen atom of the Lewis base and the oxygen atom of the TFA (IV and V) or the bromide (VI).
Salient structural features of IV–VI are listed in Table 2.1.7. In all palladacycles, the palladium atom revealed a somewhat distorted square planar geometry. The Lewis base is coordinated to the palladium atom in cis relation with respect to the Pd–C bond. The molecular structures of imine derived six-membered \([C,N]\) palladacycles of the type \([C,N]\text{PdX}(L)\] (L: phosphine\(^{4,32}\)) are known to contain the Lewis base cis to the Pd–C due to antisymbiosis. However, an unusual trans configuration was observed for the palladium atom in \([\text{Pd}\{\kappa_2(C,N)-C_6H_5(OMe)-3(\text{NHC(NHAr})(=\text{NAr})-2)\text{Br}(L)\}]\) (Ar = 2-(MeO)C\(_6\)H\(_4\); L = 2,6-Me\(_2\)C\(_5\)H\(_3\)N (35), 2,4-Me\(_2\)C\(_5\)H\(_3\)N (36)\(^{16}\) and such configuration was explained by invoking relative hardness/softness of the donor atoms surrounding the palladium and its antisymbiotic behaviour.\(^{33}\) The six-membered "\([C,N]\text{Pd}\)" ring in IV–VI adopts a pseudo boat conformation as analogously observed in 35 and 36.\(^{16}\)

Table 2.1.4 Selected Bond Distances (Å) and Bond Angles (deg) for Palladacycle IV

<table>
<thead>
<tr>
<th>Bond Distances (Å) and Bond Angles (deg) for Palladacycle IV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IV</strong> (molecule 1)</td>
</tr>
<tr>
<td>Pd(1)-C(17) 1.982(5) C(17)-Pd(1)-N(1) 90.4(2) C(8)-N(2)-C(9) 128.2(4)</td>
</tr>
<tr>
<td>Pd(1)-N(1) 2.019(4) C(17)-Pd(1)-N(4) 92.9(2) C(8)-N(3)-C(16) 127.1(4)</td>
</tr>
<tr>
<td>Pd(1)-N(4) 2.061(4) N(1)-Pd(1)-N(4) 176.1(2) C(16)-C(17)-Pd(1) 122.0(3)</td>
</tr>
<tr>
<td>Pd(1)-O(1) 2.137(3) C(17)-Pd(1)-O(1) 177.2(2) N(1)-C(8)-N(3) 122.2(4)</td>
</tr>
<tr>
<td>N(1)-C(8) 1.306(6) N(1)-Pd(1)-O(1) 91.4(1) N(3)-C(16)-C(17) 122.4(4)</td>
</tr>
<tr>
<td>N(2)-C(8) 1.370(6) N(4)-Pd(1)-O(1) 85.2(1) N(1)-C(8)-N(2) 120.6(4)</td>
</tr>
<tr>
<td>N(3)-C(8) 1.351(6) C(8)-N(1)-Pd(1) 126.4(3)</td>
</tr>
<tr>
<td>N(3)-C(16) 1.411(6)</td>
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<tr>
<td><strong>IV</strong> (molecule 2)</td>
</tr>
<tr>
<td>Pd(2)-C(48) 1.997(5) C(48)-Pd(2)-N(5) 91.1(2) C(39)-N(6)-C(40) 127.1(4)</td>
</tr>
<tr>
<td>Pd(2)-N(5) 2.025(4) C(48)-Pd(2)-N(8) 93.8(2) C(39)-N(7)-C(47) 127.6(4)</td>
</tr>
<tr>
<td>Pd(2)-N(8) 2.062(4) N(5)-Pd(2)-N(8) 174.0(2) N(5)-C(39)-N(7) 123.0(5)</td>
</tr>
<tr>
<td>Pd(2)-O(3) 2.164(3) C(48)-Pd(2)-O(3) 175.6(2) N(5)-C(39)-N(6) 121.7(5)</td>
</tr>
<tr>
<td>N(5)-C(39) 1.302(6) C(5)-Pd(2)-O(3) 91.8(1) N(7)-C(39)-N(6) 115.3(4)</td>
</tr>
<tr>
<td>N(6)-C(39) 1.373(6) N(8)-Pd(2)-O(3) 83.5(1) C(47)-C(48)-Pd(2) 122.5(4)</td>
</tr>
<tr>
<td>N(7)-C(39) 1.354(6) C(39)-N(5)-Pd(2) 126.3(3)</td>
</tr>
<tr>
<td>N(7)-C(47) 1.421(6)</td>
</tr>
</tbody>
</table>

Table 2.1.5 Selected Bond Distances (Å) and Bond Angles (deg) for Palladacycle V.

<table>
<thead>
<tr>
<th>Bond Distances (Å) and Bond Angles (deg) for Palladacycle V.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>V</strong></td>
</tr>
<tr>
<td>Pd(1)-C(17) 1.979(3) C(17)-Pd(1)-N(1) 85.0(1) C(8)-N(2)-C(9) 126.2(3)</td>
</tr>
<tr>
<td>Pd(1)-N(1) 2.098(3) C(17)-Pd(1)-O(1) 177.3(1) C(8)-N(3)-C(16) 122.1(3)</td>
</tr>
<tr>
<td>Pd(1)-O(1) 2.183(2) N(1)-Pd(1)-O(1) 93.5(1) N(1)-C(8)-N(2) 125.6(3)</td>
</tr>
<tr>
<td>Pd(1)-P(1) 2.2403(9) C(17)-Pd(1)-P(1) 90.97(9) N(1)-C(8)-N(3) 120.3(3)</td>
</tr>
<tr>
<td>N(1)-C(8) 1.323(4) N(1)-Pd(1)-P(1) 171.28(7) N(2)-C(8)-N(3) 114.0(3)</td>
</tr>
<tr>
<td>N(2)-C(8) 1.359(4) O(1)-Pd(1)-P(1) 90.18(6) C(16)-C(17)-Pd(1) 115.2(2)</td>
</tr>
<tr>
<td>N(3)-C(8) 1.364(4) C(8)-N(1)-Pd(1) 113.0(2) C(8)-N(3)-C(16) 122.1(3)</td>
</tr>
</tbody>
</table>

65
Figure 2.1.4 The ORTEP representation of IV [molecule 1 (left) and molecule 2 (right)] at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
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Figure 2.1.5 The ORTEP representation of V at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Figure 2.1.6 The ORTEP representation of VI [molecule 1 (left) and molecule 2 (right)] at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
### Table 2.1.6 Selected Bond Distances (Å) and Bond Angles (deg) for Palladacycle VI.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(1)-C(17)</td>
<td>1.983(3)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Pd(1)-N(1)</td>
<td>2.038(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(1)-N(4)</td>
<td>2.049(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(1)-Br(1)</td>
<td>2.606(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-C(8)</td>
<td>1.315(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-C(8)</td>
<td>1.358(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(8)</td>
<td>1.354(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)-Pd(1)-N(1)</td>
<td>85.57(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)-Pd(1)-N(4)</td>
<td>90.38(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)-Pd(1)-Br(1)</td>
<td>168.58(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-N(1)-Pd(1)</td>
<td>116.8(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-N(4)-Pd(1)</td>
<td>125.7(3)</td>
<td></td>
<td></td>
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<tr>
<td>N(1)-Pd(1)-N(4)</td>
<td>122.5(3)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>N(1)-Pd(1)-Br(1)</td>
<td>116.8(2)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>N(2)-Pd(1)-Br(1)</td>
<td>88.20(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(8)-N(2)</td>
<td>115.1(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(8)-N(2)</td>
<td>115.1(3)</td>
<td></td>
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</tbody>
</table>

### Table 2.1.7 Geometric Parameters of the CN₃ Core in Palladacycles IV–VI

<table>
<thead>
<tr>
<th>Parameters</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>∆CN, Å</td>
<td>0.045(8)</td>
<td>0.052(8)</td>
<td>0.041(6)</td>
</tr>
<tr>
<td>∆CN', Å</td>
<td>0.064(8)</td>
<td>0.071(8)</td>
<td>0.036(6)</td>
</tr>
<tr>
<td>Dihedral angle between &quot;NPdC&quot; plane and O–Pd–N deg</td>
<td>2.79(28)</td>
<td>5.01(16)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>O–Pd–P deg</td>
<td>–</td>
<td>8.08(9)</td>
</tr>
<tr>
<td></td>
<td>Br–Pd–N deg</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The Pd–O distance in molecule 1 (Pd–O: 2.137(3) Å) is slightly shorter than that observed in molecule 2 (2.164(3) Å) of IV and the corresponding distance observed in V (Pd–O: 2.183(2) Å). The Pd–N distances in IV (Pd–N: 2.061(4) Å (molecule 1) and 2.019(4) Å (molecule 2)) and VI (Pd–N: 2.049(2) Å (molecule 1) and 2.051(2) Å (molecule 2)) are shorter than the corresponding distance observed in 35 (2.060(4), 2.173(4) Å) and 36 (2.160(3) and 2.049(3) Å). The Pd–Br distance in VI (2.6064(4) Å (molecule 1) and 2.596(4) Å (molecule 2)) is longer than the corresponding distance observed in 35 (2.441(6) Å) and 36 (2.446(5) Å) as the bromine atom is
trans to the imine nitrogen atom in 35 and 36. The Pd–P distance in V (2.2403(9) Å) is slightly longer than that reported for PTA ligated five-membered [C,N] palladacycle (2.2260(4) Å). In palladacycles IV–VI, the amino nitrogens are planar. Molecule 1 and molecule 2 of VI are linked to each other by intermolecular N–H···Br hydrogen bonding. Each molecule is shown to possess one intramolecular C–H···Br hydrogen bonding as well (see Figure S2.1.2).

2.1.3.10 Spectroscopic Data

The IR data of IV–VII are listed in Table 2.1.8. Palladacycles IV–VII revealed two separate bands for endocyclic and exocyclic NH moieties in the interval 3232–3401 cm\(^{-1}\) and a single band in the interval 1600–1628 cm\(^{-1}\) assignable to the C=N moiety of the guanidine. Further, palladacycles IV and V revealed an intense bands at 1681 and 1673 cm\(^{-1}\) assignable to \(\nu_a(OCO)\) and a less intense band at 1470 and 1459 cm\(^{-1}\) assignable to \(\nu_s(OCO)\). The magnitude of \(\Delta \nu = \nu_a(OCO) – \nu_s(OCO)\) indicates monodentate carboxylate coordination mode. In addition, two intense bands were observed for IV (1198 and 1132 cm\(^{-1}\)) and V (1200 and 1144 cm\(^{-1}\)) assignable to C–F stretch of the CF\(_3\) unit.

| Table 2.1.8 Selected FT-IR Spectral Data for Palladacycles IV–VII (KBr, cm\(^{-1}\)) |
|---------------------------------|-----------------|---------------|----------------|----------------|----------------|-----------------|
| \(\nu(\text{NH})\)            | \(\nu(\text{C=N})\) | \(\Delta \nu(\text{C=N})^a\) | \(\nu_a(\text{OCO})\) | \(\nu_s(\text{OCO})\) | \(\Delta \nu^b\) | \(\nu(\text{CF})\) |
| IV                             | 3399, 3277      | 1628          | –13            | 1681           | 1470           | 211             | 1198, 1132      |
| V                              | 3362, 3322      | 1623          | –18            | 1673           | 1459           | 214             | 1200, 1144      |
| VI                             | 3401, 3272      | 1622          | –19            | –              | –              | –               | –               |
| VII                            | 3390, 3232      | 1600          | –41            | –              | –              | –               | –               |

\(^a\Delta \nu(\text{C=N}): \nu(\text{C=N})_{\text{complex}} – \nu(\text{C=N})_{\text{guanidine}}\), \(^b\Delta \nu = \nu_a(\text{OCO}) – \nu_s(\text{OCO})\).

The \(^1\text{H}\) NMR spectrum of IV revealed three singlets at \(\delta_\text{H} 1.98, 2.33\) and 2.38 ppm in about 1:1:1 ratio assignable to \(\text{CH}_3\) protons of the guanidine unit and another singlet at \(\delta_\text{H} 3.23\) ppm assignable to \(\text{CH}_3\) protons of 2,6-lutidine moiety. The \(^13\text{C}\) NMR spectrum of IV revealed two peaks at \(\delta_c 20.9\) and 21.1 assignable to \(\text{CH}_3\) carbon of the guanidine unit instead of three singlets due to overlap. Further, one characteristic peak was observed at \(\delta_c 27.7\) ppm assignable to \(\text{CH}_3\) carbon of 2,6-lutidine moiety. In addition, two characteristic quartets were observed at \(\delta_c 116.4\) (\(J_{\text{CF}} = 293.2\) Hz) and 160.5 (\(J_{\text{CF}} 34.5\) Hz) ppm assignable to CF\(_3\) and OCO carbon nuclei, respectively.
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Palladacycle V revealed three singlets at $\delta_H$ 2.43, 2.47 and 2.51 ppm in about 1:1:1 ratios assignable to $CH_3$ protons of the guanidine unit. Additionally, two characteristic singlets were observed at $\delta_H$ 4.28 and 4.57 ppm assignable to $PCH_2N$ and $NCH_2N$ protons of the PTA moiety. The intensity ratios of five singlets mentioned above are 3:3:6:6:6. The $^{13}C$ NMR spectrum of V also revealed two peaks at $\delta_C$ 20.8 and 20.9 ppm assignable to $CH_3$ carbon of the guanidine unit. Additionally, a pair of doublet were observed at $\delta_C$ 51.0 ($J_{CP} = 14.4$ Hz) and 73.1 ($J_{CP} = 6.7$ Hz) ppm assignable to $PCH_2N$ and $NCH_2N$ carbon nuclei of PTA, respectively.4 Further, two characteristic quartets were observed at $\delta_C$ 116.3 ($J_{CF} = 291.9$ Hz) and 161.2 ($J_{CF} = 35.1$ Hz) ppm assignable to $CF_3$ and $OCO$ carbon nuclei, respectively. The $^{19}F$ NMR spectrum of palladacycles IV and V revealed a singlet at $\delta_F$ –75.1 and –74.4 ppm, respectively. The $^{31}P$ NMR spectrum of V revealed a singlet at $\delta_P$ –51.2 ppm, and this value is slightly up field shifted than that reported for PTA ligated five-membered $[C,N]$ palladacycles ($\delta_P$ – 46.5 and – 49.6 ppm).34,35

The $^1H$ NMR spectrum of VI and VII revealed three singlets at $\delta_H$ 1.97, 2.32 and 2.36 ppm and $\delta_H$ 2.30, 2.34 and 2.36 ppm, respectively assignable to $CH_3$ carbon of the guanidine unit. Further, palladacycle VI revealed a singlet at $\delta_H$ 3.14 ppm assignable to $CH_3$ protons of 2,6-lutidine moiety. The intensity ratios of singlets of VI are 3:3:3:6. Palladacycle VII also revealed two characteristic singlets at $\delta_H$ 4.30 and 4.44 ppm assignable to $PCH_2N$ and $NCH_2N$ protons of PTA, respectively. The intensity ratios of singlets of VII are 3:3:3:6:6.

The $^{13}C$ NMR spectrum of VI revealed three singlets at $\delta_C$ 20.9, 21.0 and 21.2 ppm assignable to $CH_3$ carbon of the guanidine unit. One singlet was observed at $\delta_C$ 28.3 ppm assignable to $CH_3$ carbon of 2,6-lutidine. Palladacycle 35 was shown to exist as a mixture of two boat conformers and one planar conformer in solution as revealed by VT and VC $^1H$ NMR data.16 The $^1H$ and $^{13}C$ NMR spectra of IV and VI clearly indicated only one signal for $CH_3$ protons of lutidine and those of guanidine and only one signal for $CH_3$ carbon of lutidine and those of guanidine. The presence of one isomer of VI in solution is due the presence of more symmetrical $=N(C_6H_4Me-4)$ as compared with the less symmetrical $=N(C_6H_4(OMe)-2)$ unit in 35. The $^{13}C$ NMR spectrum of VII revealed only two peaks at $\delta_C$ 20.96 and 20.99 ppm for $CH_3$ carbon of the guanidine unit instead of anticipated three peaks due to overlap. Palladacycle VII also revealed five signals for $CH_3$ carbon of PTA unit. One would anticipate two
13C NMR signals for CH2 carbon of PTA but the reason for the observance of five signals is not clear presently. The 31P NMR spectrum of VII revealed a singlet at δp – 49.7 ppm and this value slightly shifted downfield than that reported palladacycle V but slightly up field shifted than that reported for PTA bound five-membered [C,N] palladacycles.34,35 The TOF-MS+ spectrum of palladacycles V, VI and VII revealed a peak at m/z (intensity%): 707 (18), 623.0409 (53), and 673 (15) assignable to [V + 2H]+, [VI + H]+ and [VII + H]+, respectively.

The IR spectrum of VIII revealed two bands at 3403 and 3340 cm⁻¹ assignable to two distinct NH moieties. A strong band was also observed at 1630 cm⁻¹assignable to the C= N moiety. The 1H NMR spectrum of VIII revealed two singlets at δH 1.56 and 1.98 ppm assignable to CH3 protons of acac moiety. Three characteristic singlets were observed at δH 2.31, 2.33 and 2.36 ppm assignable to CH3 protons of the guanidine unit. The intensity ratios of the above mentioned five peaks are about 1:1:1:1:1. The 13C NMR spectrum of VIII revealed three singlets at δC 21.0, 21.1 and 21.2 ppm assignable to CH3 carbons of the guanidine moiety. Additionally, two singlets were observed at δC 27.2 and 27.6 ppm assignable to CH3 carbons of the acac unit. Two peaks were observed at δC 185.7 and 187.6 ppm assignable to two distinct C=O carbons of acac and these values are comparable with those reported for the related imine derived six-membered [C,N] palladacycle (δC 187.1, and 188.2 ppm).36

2.1.4 CONCLUSION

Four classes of LH24-tolyl derived six-membered [C,N] palladacycles namely [(C,N)Pd(µ-OC(O)R)]2 (I and II), [(C,N)Pd(µ-Br)]2 (III) and [(C,N)Pd(L)(X)] (IV–VII) and [(C,N)Pd(acac)] (VIII) were isolated in good yield. Palladacycles I–VI were characterized by single-crystal X-ray diffraction data. Palladacycles I and II adopt a transoid in-in conformation in the solid state. Palladacycle III was shown to exist as a dimer and the [Pd(µ-Br)2Pd]2+ unit was shown to reveal a planar rhomboid conformation with a crystallographic C2 axis passing vertically across the centre of the ring. Palladacycles IV–VI revealed a cis configuration around the palladium atom as Lewis base is placed cis to Pd–C bond. The six-membered "[C,N]Pd" ring in IV–VI revealed a pseudo boat conformation. Palladacycles I–VIII revealed the presence of a single isomer in solution in each case due to the presence of a symmetric 4-tolyl substituent of the =NAr unit.
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2.1.5 REFERENCES

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Preparation, Structural Characterization, Catalytic Utility of \( \text{trans-[X}_2\text{Pd}(\text{LH}_2^{2,5\text{-xylyl}})_2} \) (\( \text{X} = \text{Cl and OC(O)R; R = Me, Ph, and 'Bu} \)) and \( \text{trans-[(CF}_3\text{C(O)O)}_2\text{Pd(O)(LH}_2^{2,5\text{-xylyl}})_2} \) in Heck-Mizoroki Reaction

2.2.1 ABSTRACT

Cyclometalation resistant \( \text{sym N,N',N''-tris}(2,5\text{-xylyl})\text{guanidine, ArN=C(NHAr)}_2 \) (\( \text{Ar} = 2,5\text{-Me}_2\text{C}_6\text{H}_3; \text{LH}_2^{2,5\text{-xylyl}} \)) was designed, isolated in 85% yield and characterized by microanalytical, IR, mass spectral data, NMR (\(^1\text{H, and } ^{13}\text{C}) \) data, and single crystal X-ray diffraction data. \( \text{LH}_2^{2,5\text{-xylyl}} \) was shown to possess \( \text{anti-anti \alpha\alpha\beta/\beta\alpha\beta} \) conformation in the solid state. The reaction of \( \text{trans-[Cl}_2\text{Pd(PhCN)}_2 \) and \( \text{Pd(OC(O)R)}_2 \) with two equiv of \( \text{LH}_2^{2,5\text{-xylyl}} \) carried out separately in toluene under reflux condition for 12 h afforded \( \text{trans-[Cl}_2\text{Pd(ArN=C(NHAr)}_2 \) (\( \text{Ar} = 2,5\text{-Me}_2\text{C}_6\text{H}_3; \text{X} = \text{Cl (IX), OC(O)R; R = Me (X), Ph (XI), and 'Bu (XII)} \)) and palladium(IV) oxo guanidine complex, \( \text{[(CF}_3\text{C(O)O)}_2\text{Pd(O)(ArN=C(NHAr)}_2 \) (XIII) in > 90% yield. Adducts IX–XII and palladium(IV) oxo guanidine complex, XIII were characterized by microanalytical, IR, NMR (\(^1\text{H, and } ^{13}\text{C}) \) data and single crystal X-ray diffraction data. The stereochemical information around the square planar palladium, the disposition of the C=N double bond of the one guanidine with respect to the C=N double bond of the other guanidine, orientation of the xylyl moiety of the –NHAr units with respect to the C=N unit of the guanidine, and orientation of o-Me substituent of the xylyl substituent with respect of plane of the CN\(_3\) unit were analyzed and turn out to be \( \text{trans syn anti-anti \alpha\alpha\beta/\beta\alpha\beta} \) (IX), \( \text{trans anti anti-syn \beta\alpha\beta/\alpha\beta\alpha} \) (X), \( \text{trans anti anti-syn \beta\beta\beta/\alpha\alpha\alpha} \) (XI), and \( \text{trans anti anti-anti \beta\beta\alpha/\alpha\alpha\beta} \) (XII). The palladium atom in the adduct XIII revealed a square pyramidal geometry with two basal positions occupied by the oxygen atom of the monodentate trifluoroacetate moiety in \( \text{trans} \) disposition as was the imine nitrogen atom of the guanidine unit and the apical position was occupied by the oxo ligand. In solution, adducts IX and XII were shown to exist as a single isomer whereas X and XI were shown to exist as a mixture of two isomers in about 1:1 ratio as revealed by room
temperature $^1$H and $^{13}$C NMR data and a variable temperature $^1$H NMR data and NOESY NMR data measured at 243 K in the case of XI. Adducts X and XI in solution were shown to exist as a mixture of trans anti anti-syn and trans anti anti-anti isomers and were shown to interconvert via the restricted C–N(H)Ar bond rotation. Adducts IX–XIII were shown to be effective precatalysts for Heck coupling reaction involving chlorobenzene and methylacrylate.

2.2.2 INTRODUCTION

Trans-[Cl$_2$Pd(imine)$_2$] adducts are one of the interesting classes of coordination compounds and can exist in two different rotameric forms namely trans syn and trans anti due to two distinct orientations of the C=N unit with respect to each other. The interconversion of the aforementioned forms was ascribed to arise from the Pd–N bond rotation as demonstrated for trans-[Cl$_2$Pd(R$_2$NN=CR$_2$)$_2$].$^{1,2}$ This class of adducts is anticipated to replace the conventional palladium phosphine complexes as precatalysts in homogeneous catalysis$^3$ and is being used as precatalysts in cross coupling reactions.$^4$ We have been studying the coordination chemistry aspects of sym N,N',N″-triarylguanidines, ArN=C(NHAr)$_2$ (Ar = tolyl, anisyl, and xylyl) towards platinum group metals (Ru, Os, Rh, Ir, Pd and Pt) with a view aimed at understanding the solid state structure and solution behavior of the resulting complexes and to further explore the catalytic utility of these complexes in cross coupling reactions.$^5$ N. Mincheva et al have reported the molecular structure of trans-[Cl$_2$Pd((PhN=C(NHPh)$_2$)$_2$] and in this complex, two C=N double bonds are placed cis to each other (i.e. syn) and the guanidine was shown to reveal trans syn syn-anti/anti-anti conformation in the solid state.$^6$ Other palladium(II) guanidine adducts of the type trans-[(guanidine)$_2$PdCl$_2$] are known and some of them have been shown to act as an excellent precatalysts for cross coupling reactions.$^7$–$^{10}$

We have intended to prepare trans-[X$_2$Pd(ArN=C(NHAr)$_2$)] (Ar = 2,5-Me$_2$C$_6$H$_3$; X = Cl (IX), OC(O)R; R = Me (X), Ph (XI), tBu (XII) and CF$_3$ (XIII′)) and to investigate how systematic change of X influences the solid state structure and solution behavior of this class of adducts. We chose sym N,N',N″-tris(2,5-xylyl)guanidine, ArN=C(NHAr)$_2$ (Ar = 2,5-Me$_2$C$_6$H$_3$; LH$_2^{2,5}$-xylyl) for the job at hand because the methyl substituent in the
5th position of xylyl ring would avoid cyclometalation upon reaction with palladium precursors\(^\text{11}\) and thus a more robust 1:2 adducts of the type IX–XIII would form rather than guanidine derived six-membered \([C,N]\) palladacycles, \([\text{Pd}\{κ^2(C,N)-C_6H_3Me_2-3,6(NHC(NHAr)(=NAr))-2\}](µ-OC(O)R)\) \((\text{Ar} = 2,5-\text{Me}_2\text{C}_6\text{H}_3)\). It is to be noted that sym \(N,N',N''\)-tri(2-tolyl)guanidine, \(\text{ArN}=\text{C}(\text{NHAr})_2\) upon reaction with \(\text{Pd(OAc)}_2\) in 1:2 ratio even at 15 °C was shown to afford a mixture of \(\text{trans-}[\text{AcO}_2\text{Pd}(\text{ArN}=\text{C}(\text{NHAr})_2)]\), \([\text{Pd}\{κ^2(C,N)-C_6H_3Me-5(\text{NHC(NHAr})(=NAr))-2\}(µ-\text{OAc})_2\] \((\text{Ar} = 2-\text{MeC}_6\text{H}_4)\) in 60 and 13% yield, respectively rather than exclusive formation of the adduct.\(^\text{12}\)

We report herein the synthesis, solid state structural aspects and solution behavior of adducts, IX–XII. The low temperature X-ray diffraction data of the trifluoroacetate adduct indicated the formation of a rare palladium(IV) guanidine oxo adduct, XIII rather than the anticipated 1:2 adduct, XIII' (see Chart 2.2.1). Further, adducts, IX–XIII were shown to be effective precatalysts for Heck coupling reaction of chlorobenzene with methylacrylate.

**Chart 2.2.1**

\[
\text{IX} \quad \text{X} = \text{OC(O)R} \\
\text{R} = \text{Me} (\text{X}) ; \text{Ph} (\text{XI})
\]

\[
\text{X} = \text{OC(O)\text{tBu} (XII)} \\
\text{X} = \text{OC(O)CF}_3 (\text{XIII}) ; \text{E} = \text{O} \\
\text{X} = \text{OC(O)CF}_3 (\text{XIII'}) ; \text{E} = \text{none}
\]

\(\text{Ar} = 2,5-\text{Me}_2\text{C}_6\text{H}_3\)
2.2.3 RESULTS AND DISCUSSION

2.2.3.1 Sym $N,N',N'''\text{tris}(2,5\text{-xylyl})\text{guanidine}$, $ArN=C(NHAr)_2$ (Ar = $2,5\text{-Me}_2C_6H_3$; LH$_2^{2,5\text{-xylyl}}$)

The reaction of sym $N,N'-\text{bis}(2,5\text{-xylyl})\text{ thiourea}$, (ArNH)$_2$C=S with ArNH$_2$ in nitrobenzene at 110 °C for 8 h following the procedure previously published for the related guanidines$^{13}$ afforded sym $N,N',N'''\text{tris}(2,5\text{-xylyl})\text{guanidine}$, $ArN=C(NHAr)_2$ (Ar = $2,5\text{-Me}_2C_6H_3$; LH$_2^{2,5\text{-xylyl}}$) in 85% yield as illustrated in Scheme 2.2.1. LH$_2^{2,5\text{-xylyl}}$ was characterized by IR, NMR ($^1H$, and $^{13}C$), ESI-MS, microanalytical data and single crystal X-ray diffraction data.

**Scheme 2.2.1** Synthesis of sym $N,N',N'''\text{tris}(2,5\text{-xylyl})\text{guanidine}$, LH$_2^{2,5\text{-xylyl}}$

LH$_2^{2,5\text{-xylyl}}$ was crystallized from hot ethanol at ambient temperature over a period of several hours and the material crystallized in triclinic $P\bar{1}$ space group. The molecular structure of LH$_2^{2,5\text{-xylyl}}$ is illustrated in Figure 2.2.1. Selected bond distances and bond angles are listed in Table 2.2.1. Guanidine, LH$_2^{2,5\text{-xylyl}}$ revealed *anti-anti* $\alpha\alpha\beta\beta$ conformation ($\tau_{(CNC-CN)}$: 135.8(2) and 150.0(2)$^\circ$). The values of $\Delta CN$: 0.096(2) Å and $\Delta CN'$: 0.098(3) Å in LH$_2^{2,5\text{-xylyl}}$ are comparable with the corresponding values observed for LH$_2^{2,4\text{-xylyl}}$ ($\Delta CN$: 0.091(3) Å and $\Delta CN'$: 0.108(3) Å)$^{13}$ and LH$_2^{2,6\text{-xylyl}}$ ($\Delta CN$: 0.083(6) Å and $\Delta CN'$: 0.090(6) Å)$^{14}$. Both the amino nitrogens deviate slightly from planarity ($\Sigma N$: 350 and 354$^\circ$). The reference molecule is linked to the inversion related neighboring molecule.
by a pair of intramolecular N–H···N hydrogen bonding to afford a dimer as illustrated in Figure S2.2.1. In addition, two halves of the dimer is linked to each other by two pairs of C–H···π interaction.

**Figure 2.2.1** The ORTEP representation of LH\textsubscript{2,5-xylyl} at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.

**Table 2.2.1** Selected Bond Distances (Å) and Bond Angles (deg.) for LH\textsubscript{2,5-xylyl}.

<table>
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<th>LH\textsubscript{2,5-xylyl}</th>
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<tbody>
<tr>
<td>N(1)-C(1)</td>
<td>1.279(2)</td>
<td>C(1)-N(1)-C(2)</td>
<td>120.0(1)</td>
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<td>N(1)-C(2)</td>
<td>1.414(2)</td>
<td>C(1)-N(2)-C(10)</td>
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<td>N(2)-C(1)</td>
<td>1.375(2)</td>
<td>C(1)-N(3)-C(18)</td>
<td>123.9(2)</td>
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<td>N(2)-C(10)</td>
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<td>N(1)-C(1)-N(2)</td>
<td>119.4(1)</td>
</tr>
<tr>
<td>N(3)-C(1)</td>
<td>1.377(2)</td>
<td>N(1)-C(1)-N(3)</td>
<td>124.7(2)</td>
</tr>
<tr>
<td>N(3)-C(18)</td>
<td>1.421(2)</td>
<td>N(2)-C(1)-N(3)</td>
<td>115.9(1)</td>
</tr>
</tbody>
</table>
Chapter 2: Results and Discussion

The IR spectrum of \( \text{LH}_2^{2,5-\text{xylyl}} \) revealed two bands at 3431 and 3367 cm\(^{-1} \) assignable to two distinct NH moieties. Further, a characteristic band was observed at 1654 cm\(^{-1} \) assignable to the C=N moiety. The \(^1\)H NMR spectrum of \( \text{LH}_2^{2,5-\text{xylyl}} \) revealed two singlets at \( \delta \) \( \text{H} = 2.14 \) and 2.27 ppm assignable to two distinct \( \text{CH}_3 \) protons of the xylyl ring. Two broad signals were observed at \( \delta \) \( \text{H} = 5.56 \) and 7.33 ppm assignable to two distinct NH protons. The \(^{13}\)C NMR spectrum of \( \text{LH}_2^{2,5-\text{xylyl}} \) revealed two singlets at \( \delta \) \( \text{C} = 17.5 \) and 21.2 ppm assignable to two distinct \( \text{CH}_3 \) carbon of the xylyl moiety. The aryl carbon of \( \text{LH}_2^{2,5-\text{xylyl}} \) revealed seven peaks in the interval \( \delta \) \( \text{C} = 122.5–144.8 \) ppm assignable to the C=N and ArC carbons of guanidine moiety. ESI-MS spectrum of \( \text{LH}_2^{2,5-\text{xylyl}} \) revealed two peaks at m/z (intensity %): 372.7982 (94) and 371.2616 (89) assignable to \([\text{M} + \text{H}]^+\) and \([\text{M}]^+\), respectively.

2.2.3.2 1:2 Palladium(II) Guanidine Adducts

2.2.3.2.1 Synthesis

The reaction of \( \text{trans-[Cl}_2\text{Pd(PhCN)}_2\text{]} \) with \( \text{LH}_2^{2,5-\text{xylyl}} \) in 1:2 mole ratio in toluene under reflux condition for 12 h afforded \( \text{trans-[Cl}_2\text{Pd(ArN=C(NHAr)}_2\text{)]} \) (Ar = 2,5-Me\(_2\)C\(_6\)H\(_3\); IX) as orange red crystals in 93% yield. The reaction of Pd(O(C)R)\(_2\) with \( \text{LH}_2^{2,5-\text{xylyl}} \) in 1:2 mole ratio in toluene under reflux condition for 12 h afforded \( \text{trans-[(R(O)CO)}_2\text{Pd(ArN=C(NHAr)}_2\text{)]} \) (Ar = 2,5-Me\(_2\)C\(_6\)H\(_3\); R = Me (X), Ph (XI), and tBu (XII)) as orange crystals in 95–96% yield. These transformations are illustrated in Scheme 2.2.2. It is to be noted that the reaction of Pd(OAc)\(_2\) with \( \text{LH}_2^{2,5-\text{xylyl}} \) in 1:1 mole ratio in toluene under reflux condition for 6 h lead to the formation of X instead of anticipated palladacycle, \([\text{Pd}\{\kappa^2(C,N)-C_6H_2Me_2-3,6(NHC(NHAr)(=NAr))-2\}(\mu-OAc)}]_2 \) (Ar = 2,5-Me\(_2\)C\(_6\)H\(_3\)). The resistance of \( \text{LH}_2^{2,5-\text{xylyl}} \) for cyclometalation could be ascribed to the presence of methyl substituent in the 5\(^{th}\) position of one of the NHAr moieties. The source of oxygen in XIII is believed to be atmospheric oxygen.

2.2.3.2.2 Solid State Structural Aspects

Adducts IX–XII was crystallized from toluene/CHCl\(_3\) mixture at ambient temperature over a period of several days. Adducts IX, X and XI crystallized as
Chapter 2: Results and Discussion

IX-CHCl₃, X-CHCl₃ and XI-C₇H₈ while XII crystallized without any solvent molecule in the crystal lattice. The molecular structures of IX, X and XI, and XII are illustrated in Figures 2.2.2–2.2.5, respectively. Selected bond parameters are listed in Tables 2.2.2–2.2.5, respectively. The palladium atom in X and XI was located on an inversion symmetry and hence two halves of the molecule are related by a center of symmetry. The palladium atom in these compounds is surrounded by imine nitrogen atom of two guanidines placed in a mutually opposite position as are two chlorides (IX) or oxygen atom of two monodentate carboxylate moieties (X and XI, and XII).

**Scheme 2.2.2 Synthesis of 1:2 Palladium(II) Guanidine Adducts of LH₂²⁻xylyl.**

In principle, IX–XII can exist as (i) trans syn syn-syn, (ii) trans syn syn-anti, (iii) trans syn anti-syn, (iv) trans syn anti-anti, (v) trans anti syn-syn, (vi) trans anti syn-anti, (vii) trans anti anti-syn, and (viii) trans anti anti-anti conformers as shown in Chart 2.2.2. In this nomenclature, the first word refers to the geometry of the palladium atom, second word refers to the orientation of the C=N double bond of one guanidine with respect to the C=N double bond of the second guanidine, and the pair of third words indicate orientation of the xyllyl moiety of NHAr units with respect to the C=N double bond of the guanidine as discussed previously for *sym N,N'-N'-*triarylguanidines.¹³
Figure 2.2.2 The ORTEP representation of IX at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Figure 2.2.3 The ORTEP representation of X the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Figure 2.2.4 The ORTEP representation of XI at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Figure 2.2.5 The ORTEP representation of XII at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
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Table 2.2.2 Selected Bond Distances (Å) and Bond Angles (deg.) of 1:2 Adduct IX.

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<tr>
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<th>Bond Distances (Å)</th>
<th>Bond Angles (deg.)</th>
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<tr>
<td>Pd1-C1</td>
<td>2.308(6)</td>
<td>N1-Pd1-N4</td>
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<tr>
<td>Pd1-C2</td>
<td>2.323(6)</td>
<td>N1-Pd1-C11</td>
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<td>Pd1-N1</td>
<td>2.024(2)</td>
<td>N1-Pd1-Cl2</td>
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<td>Pd1-N4</td>
<td>2.035(2)</td>
<td>Cl1-Pd1-N4</td>
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<td>N1-C1</td>
<td>1.304(3)</td>
<td>Cl2-Pd1-N4</td>
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<td>C1-N2</td>
<td>1.373(3)</td>
<td>Cl1-Pd1-Cl2</td>
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<td>C1-N3</td>
<td>1.353(3)</td>
<td>C1-N2-C10</td>
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<tr>
<td>C26-N4</td>
<td>1.298(3)</td>
<td>C1-N3-C18</td>
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<td>N5-C26</td>
<td>1.380(3)</td>
<td>C26-N5-C35</td>
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<tr>
<td>N6-C26</td>
<td>1.357(3)</td>
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Table 2.2.3 Selected Bond Distances (Å) and Bond Angles (deg.) of 1:2 Adduct X.

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<td>Pd1-O1</td>
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<td>Pd1-N1</td>
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Table 2.2.4 Selected Bond Distances (Å) and Bond Angles (deg.) of 1:2 Adduct XI.

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<td>Pd(1)-O(1)</td>
<td>2.016(2)</td>
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<td>C(26)-O(1)-Pd(1)</td>
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Table 2.2.5 Selected Bond Distances (Å) and Bond Angles (deg.) of 1:2 Adduct XII.

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<td>Pd(1)-O(1)</td>
<td>2.017(1)</td>
<td>O(1)-Pd(1)-O(3)</td>
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<td>Pd(1)-O(3)</td>
<td>2.019(1)</td>
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<td>O(3)-Pd(1)-N(4)</td>
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<td>O(3)-Pd(1)-N(1)</td>
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<td>O(2)-C(51)</td>
<td>1.236(2)</td>
<td>N(4)-Pd(1)-N(1)</td>
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<td>1.285(2)</td>
<td>C(1)-N(2)-C(10)</td>
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<tr>
<td>O(4)-C(56)</td>
<td>1.237(2)</td>
<td>C(1)-N(3)-C(18)</td>
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<tr>
<td>N(1)-C(1)</td>
<td>1.316(2)</td>
<td>C(26)-N(5)-C(35)</td>
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<td>N(2)-C(1)</td>
<td>1.347(2)</td>
<td>C(26)-N(6)-C(43)</td>
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<td>N(3)-C(1)</td>
<td>1.361(2)</td>
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<td>N(4)-C(26)</td>
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<tr>
<td>N(5)-C(26)</td>
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<tr>
<td>N(6)-C(26)</td>
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</table>

As per this nomenclature adduct IX revealed trans syn anti-anti ααβ/βαβ conformation, adduct X revealed trans anti anti-syn βαβ/αβα (X) conformation, adduct XI revealed trans anti anti-syn βββ/ααα conformation and adduct XII revealed trans anti anti-anti ββα/ααβ conformation. The overall stereochemistry of the related adduct, [Cl₂Pd(PhN=C(NHPh)₂)₂] is trans syn anti/anti-anti as two halves of the molecule are not related by any crystallographic symmetry as revealed by X-ray diffraction data.⁶

The salient structural features of IX–XII are listed in Table 2.2.6. The palladium atom in X and XI is shown to possess a square planar geometry whereas that in XII is shown to deviate slightly from the square planar geometry while that in IX is shown to deviate significantly from square planar geometry as revealed by the dihedral angle between two planes constituted by "PdClNimine" unit. The aforementioned dihedral angles are 9.47(11), 9.45(11)° (IX), 0.00(9)° (X), 0.00(12)° (XI), and 2.73(9), 2.75(9)° (XII). The presence of two sterically encumbered guanidines on the same side in IX or the mutual repulsive interaction between the sterically hindered 1′Bu substituent and the guanidine moiety in XII could be the reason for the deviation of the palladium atom from the ideal square planar geometry in these adducts. The dihedral angle between the CN₃ plane and the palladium square plane in IX (78.61(7) and 73.58(6)°), X (84.10(7)°), XI (83.69(8)°), and XII (85.98(7) and 86.57(6)°).
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Chart 2.2.2 Eight Possible Conformers of IX–XII

- trans syn syn-syn
- trans syn syn-anti
- trans syn anti-syn
- trans syn anti-anti
- trans anti syn-syn
- trans anti syn-anti
- trans anti anti-syn
- trans anti anti-anti
Table 2.2.6: Salient Structural Features of Adducts IX–XII

<table>
<thead>
<tr>
<th>Features</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
<th>XII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry of the palladium center</td>
<td>trans</td>
<td>trans</td>
<td>trans</td>
<td>trans</td>
</tr>
<tr>
<td>Relative disposition of the C=N unit</td>
<td>syn</td>
<td>anti</td>
<td>anti</td>
<td>anti</td>
</tr>
<tr>
<td>Conformation of the guanidine</td>
<td>anti-anti</td>
<td>anti-syn</td>
<td>anti-syn</td>
<td>anti-anti</td>
</tr>
<tr>
<td>Angle between &quot;PdXN&quot; planes (deg.)</td>
<td>9.47(11)</td>
<td>0.00(9)</td>
<td>0.00(12)</td>
<td>2.73(9)</td>
</tr>
<tr>
<td>Angle between the CN₃ plane and Pd square plane (deg.)</td>
<td>78.61(7)</td>
<td>84.10(7)</td>
<td>83.69(8)</td>
<td>85.98</td>
</tr>
<tr>
<td>(\Delta CN, \text{Å})</td>
<td>0.069(4)</td>
<td>0.043(3)</td>
<td>0.051(4)</td>
<td>0.031(3)</td>
</tr>
<tr>
<td>(\Delta CN', \text{Å})</td>
<td>0.082(4)</td>
<td></td>
<td>0.045(3)</td>
<td></td>
</tr>
<tr>
<td>(\rho)</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
</tr>
</tbody>
</table>

The amino nitrogens are planar in adducts. \(\Delta CN\): 0.096(2) Å; \(\Delta CN'\): 0.098(3) Å, and \(\rho\): 0.93 for \(LH₂²,⁵\text{-xylyl}\).

The Pd–N distance in IX (2.024(2), 2.035(2)Å), X (2.033(1) Å), XI (2.031(2) Å), and XII (2.028(2), 2.025(2) Å) are slightly shorter than the predicted value of 2.09 Å (Covalent radius, \(r(Pd(II))\): 1.39 Å; \(r(N)\): 0.70 Å)\(^{15}\) and this could be ascribed to \(\sigma\)-donor/\(\pi\)-acceptor characteristics of the imine functionality in these adducts. The values of \(\Delta CN\) and \(\Delta CN'\) in IX (\(\Delta CN\): 0.069(4), 0.082(4) Å; \(\Delta CN'\): 0.049(4), 0.059(4) Å), X (\(\Delta CN\): 0.043(3) Å; \(\Delta CN'\): 0.047(3) Å), XI (\(\Delta CN\): 0.051(4) Å; \(\Delta CN'\): 0.036(4) Å), and XII (\(\Delta CN\): 0.031(3), 0.043(3) Å; \(\Delta CN'\): 0.045(3), 0.047(3) Å) are significantly smaller than that observed for \(LH₂²,⁵\text{-xylyl}\) (\(\Delta CN\): 0.096(2) Å; \(\Delta CN'\): 0.098(3) Å). The \(\rho\) value reflects elongation of the C=N bond upon protonation, alkylation, or coordination relative to the concomitant shortening of the average C–N(H)Ar distance. The \(\rho\) value of 1.00 indicates
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a complete n–π conjugation and deviation from this value indicates impediment to the n–π conjugation.\textsuperscript{16} The $\rho$ values of IX (0.96 and 0.95), X (0.97), XI (0.97), and XII (0.97 and 0.97) are greater than the corresponding value observed for LH\textsubscript{2,5-xylyl} ($\rho$: 0.93). Unlike LH\textsubscript{2,5-xylyl}, the amino nitrogens in adducts are planar ($\Sigma N \approx 360^\circ$). The aforementioned structural parameters suggest that n–π conjugation has improved significantly in adducts relative to LH\textsubscript{2,5-xylyl} due to coordination of the imine nitrogen to the palladium atom in the former.

Adducts IX–XII possess hydrogen bond donor in the form of NH protons and hydrogen bond acceptor in the form of chloride and carbonyl oxygen. Hence, an interesting hydrogen bonding pattern is observed in the crystal lattice. The noncovalent interactions in adducts IX–XII are illustrated in Figure S2.2.2–S2.2.6. The chloride, Cl\textsubscript{1} in Figure S2.2.2 simultaneously forms a bifurcated intramolecular N–H⋯Cl and C–H⋯Cl hydrogen bonding while the chloride, Cl\textsubscript{2} simultaneously forms a pair of C–H⋯Cl and a N–H⋯Cl hydrogen bonding. The C–H⋯Cl hydrogen bonding is of both intramolecular type and intermolecular type involving CHCl\textsubscript{3}. The carbonyl oxygen, O\textsubscript{2} in X acts as a bifurcated acceptor by simultaneously forming a pair of intramolecular N–H⋯O hydrogen bonding and an intermolecular C–H⋯O hydrogen bonding with CHCl\textsubscript{3}. The carbonyl oxygen, O\textsubscript{2} and its inversion related counterpart in X and O\textsubscript{2} and O\textsubscript{4} in XII form a pair of intramolecular N–H⋯O hydrogen bonding with the protons of one of the NHAr units.

\textbf{2.2.3.2.3 Spectroscopic Data}

FT–IR data of adducts IX–XII are listed in Table 2.2.7. Adducts IX–XI revealed two bands in the range 3127–3400 cm\textsuperscript{-1} while the adduct XII revealed one band at 3379 cm\textsuperscript{-1} assignable to the NH moieties and an intense band in the range 1584–1607 cm\textsuperscript{-1} for the C=N moiety. The $\nu$(C=N) value of IX–XII are shifted to a lower wave number as compared with that observed for LH\textsubscript{2,5-xylyl}. This trend indicates coordination of the guanidine to the palladium atom through the imine nitrogen.\textsuperscript{17} The carboxylate moiety in IX–XII revealed one band in the 1625–1637 cm\textsuperscript{-1} range assignable to $\nu_a$(OCO) and one
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band in the 1370–1395 cm\(^{-1}\) range assignable to \(v_\text{s} (\text{OCO})\). The value of \(\Delta v = v_\text{a} (\text{OCO}) - v_\text{s} (\text{OCO})\) for \(X\) (247 cm\(^{-1}\)), \(XI\) (267 cm\(^{-1}\)), and \(XII\) (234 cm\(^{-1}\)) indicates a monodentate carboxylate coordination mode.\(^{18}\) ESI-MS spectrum of adducts IX–XII revealed three peaks at \(m/z = 847, 373,\) and 372 assignable to \([M - 2 X]^+\) (\(X = \text{Cl and OC(O)R; R} = \text{Me, Ph, and } t\text{Bu}\), \([\text{LH}_2^{2,5-\text{xylyl}}]^+\), and \([\text{LH}_2^{2,5-\text{xylyl}}]\), respectively.

Table 2.2.7 Selected IR Data for Adducts IX–XII (KBr, cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Adduct</th>
<th>(v(\text{NH}))</th>
<th>(v(\text{C=\text{N}}))</th>
<th>(\Delta v^a)</th>
<th>(v_\text{a} (\text{OCO}))</th>
<th>(v_\text{s} (\text{OCO}))</th>
<th>(\Delta v^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>3400, 3243</td>
<td>1600</td>
<td>-54</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X</td>
<td>3375, 3127</td>
<td>1607</td>
<td>-47</td>
<td>1625</td>
<td>1378</td>
<td>247</td>
</tr>
<tr>
<td>XI</td>
<td>3424, 3392</td>
<td>1584</td>
<td>-70</td>
<td>1637</td>
<td>1370</td>
<td>267</td>
</tr>
<tr>
<td>XII</td>
<td>3379</td>
<td>1603</td>
<td>-51</td>
<td>1629</td>
<td>1395</td>
<td>234</td>
</tr>
</tbody>
</table>

\(^a\) \(v(\text{C=\text{N}})\)\_\text{adduct} - \(v(\text{C=\text{N}})\)\_\text{guanidine}; \(v(\text{C=\text{N}}): 1654 \text{ cm}^{-1}\) for \([\text{LH}_2^{2,5-\text{xylyl}}]\).

\(^b\) \(\Delta v = v_\text{a} (\text{OCO}) - v_\text{s} (\text{OCO})\)^\(^18\)

Adducts IX and XII were shown to exist as a single isomer whereas X and XI were shown to exist as a mixture of two isomers in solution as revealed by \(^1\text{H} \text{NMR data}. \text{A two-dimensional NOESY NMR was recorded for IX to gain an insight concerning the nature of solution conformers and to unambiguously assign the signals of NH protons (see Figures 2.2.6–2.2.8). The NH protons that revealed a sharp singlet at \(\delta_H 5.58 \text{ ppm}\) was shown to have correlations with two \(\text{CH}_3\) protons (\(\delta_H 1.91\) and 2.41 ppm) as well as with the second NH proton (\(\delta_H 8.40 \text{ ppm}\) but the latter NH proton did not reveal correlation with any of the \(\text{CH}_3\) protons. Therefore, the signal at \(\delta_H 5.58 \text{ ppm}\) is assigned to \(\text{N(H3)}\) proton and this proton probably approaches closer to the protons of C8 due to either C1–N3(\(H3)\) bond rotation or due to =\(\text{N–C(aryl)}\) bond rotation. The signal at \(\delta_H 8.40 \text{ ppm}\) is assigned to \(\text{N(H2)}\) protons and there appears occur N2–C10(aryl) bond rotation so that C16 would be placed farther away from \(\text{H2}\) proton. The non-bonded distances between NH protons and \(o-\text{CH}_3\) protons are given below (see Table 2.2.8).

Table 2.2.8 Non-bonded H⋯H contacts (Å) between NH protons and \(\text{CH}_3\) protons in IX

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2⋯H16A</td>
<td>2.253</td>
</tr>
<tr>
<td>H3⋯C24</td>
<td>2.351</td>
</tr>
<tr>
<td>H3⋯C8</td>
<td>3.401</td>
</tr>
</tbody>
</table>
Figure 2.2.6 A two-dimensional NOESY NMR (400 MHz, CDCl$_3$) spectrum of IX at 298 K.
Figure 2.2.7 Expansion of the 2D NOESY NMR (400 MHz, CDCl$_3$) spectrum of IX measured at 298 K in the 5.0–9.0 ppm region versus 5.0–9.0 ppm region.
Figure 2.2.8 Expansion of the 2D NOESY NMR (400 MHz, CDCl₃) spectrum of IX measured at 298 K in the 1.0–3.1 ppm region versus 3.0–8.0 ppm region.
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A variable temperature (VT) $^1$H NMR data was recorded for IX to better understand the solution behavior of this adduct. The presence of two isomers in about 4:1 ratio was apparent at temperatures $\leq 253$ K as can be found from the signals of $CH_3$ and $NH$ protons. Totally 12 signals were observed at $\delta_H$ 1.75, 1.88, 1.92, 2.02, 2.07, 2.09, 2.13, 2.26, 2.29, 2.36, 2.38 and 2.41 ppm assignable to $CH_3$ protons and four singlets were observed at $\delta_H$ 5.52, 5.55, 8.22 and 8.39 ppm assignable to $NH$ protons of the guanidine (see Figures 2.2.9 and 2.2.10). The free energy of activation, $\Delta G^\#$: 16.3 kcal/mol measured at coalescence temperature, $T_c = 253$ K with $\Delta \nu = 0.008$ Hz is slightly smaller than that reported for $sym \, N,N'$-diarylthiourea ($\Delta G^\# = 10.5–20.9$ kcal/mol). The greater $\Delta G^\#$ value for IX as compared with $sym \, N,N'$-diarylthiourea is ascribed to greater steric crowding in IX. The presence of one major isomer and one minor isomer at temperature $\leq 253$ K was ascribed to presence of $trans \, syn \, anti$-$anti$ and $trans \, syn \, anti$-$syn$ isomer with the former predominating. The $C$–$N(H)$Ar single bond rotation of $trans \, syn \, anti$-$anti$ isomer is probably caused by mutual repulsive interaction between the xylyl moiety of two $N(H)$Ar units while the $C$–$N(H)$Ar single bond rotation in $trans \, syn \, anti$-$syn$ isomer is caused by the mutual repulsive interaction between the xylyl moiety of one of the $N(H)$Ar units and that of $=NAr$ unit and thus leads to an equilibrating mixture of two isomers as illustrated in Scheme 2.2.3. In an hypothetical $trans \, syn$ $syn$-$syn$ and $trans \, syn$ $syn$-$anti$ conformers, there would be an unfavorable repulsive interaction between the xylyl moiety of one of the $N(H)$Ar units of one guanidine with the xylyl moiety of the identical $N(H)$Ar unit of the second guanidine. Additionally, there would be a mutual repulsive interaction between the xylyl moiety of $=NAr$ unit of one guanidine with the xylyl moiety of $=NAr$ unit of the other guanidine. Hence, the formation of $trans \, syn$ $syn$-$syn$ and $trans \, syn$ $syn$-$anti$ conformers is unlikely for IX in solution.

The adduct XI was subjected to a VT $^1$H NMR study (313–213 K, CD$_2$Cl$_2$, 400 MHz) in order to gain an insight concerning the nature of solution conformers. The stack plot for $CH_3$ protons of the guanidine is illustrated in Figure 2.2.11. At 293 K, eight singlets were observed at $\delta_H$ 1.70, 1.91, 1.94, 2.06, 2.14, 2.18, 2.26, and 2.41 ppm in about 1.5:1.5:1.0:1.0:1.0:1.0:1.0:1.0 ratios, respectively assignable to $CH_3$ protons of the guanidine. At 283 K, twelve singlets were observed at $\delta_H$ 1.68, 1.70, 1.90, 1.92, 1.93,
Figure 2.2.9 A VT $^1$H NMR (400 MHz, CDCl$_3$) spectrum of IX shown in the region of 1.45–2.50 ppm for CH$_3$ protons
Figure 2.2.10 A VT $^1$H NMR (400 MHz, CDCl$_3$) spectrum of IX shown in the region of 5.10–8.70 ppm for NH and ArH protons
1.94, 2.04, 2.05, 2.13, 2.18, 2.25, and 2.41 ppm, respectively in equal intensity ratio assignable to CH$_3$ protons of the guanidine. Two pairs of singlets were observed at $\delta_{H}$ 5.41, 5.48, 11.09 and 11.11 ppm at temperatures $\leq$ 283 K assignable to two distinct NH protons of two conformers. The presence of two species at temperatures $\leq$ 283 K was ascribed to the formation of trans anti anti-syn and trans anti anti-anti conformers and this interconversion occurs through the restricted C–N(H)Ar single bond rotation as illustrated in Scheme 2.2.4. The mutual repulsive interaction between the xylyl substituent of =NAr unit and one of the N(H)Ar units in the former conformer or the mutual repulsive interaction between the xylyl substituent of two N(H)Ar units in the latter conformer facilitates the equilibrium illustrated in Scheme 2.2.4. In an hypothetical trans anti syn-syn and trans anti syn-anti conformers, there would be an unfavorable repulsive interaction between the xylyl moiety of one of the N(H)Ar units of one guanidine with the xylyl moiety of =NAr unit of the second guanidine. Hence, the formation of trans anti syn-syn and trans anti syn-anti conformers is unlikely in solution. The free energy of activation, $\Delta G^\ddagger$: 14.8 kcal/mol calculated at coalescence temperature, Tc = 283 K with $\Delta v = 0.014$ Hz is slightly smaller than that found for IX.

A two-dimensional NOESY NMR was recorded for XI at 243 K in order to gain an insight concerning the nature of solution conformers. The NOESY spectrum of XI is shown in Figure 2.2.12. A portion of NOESY NMR that connects the signals of NH protons with those of CH$_3$ protons are illustrated in Figures 2.2.13 and 2.2.14. The singlet at $\delta_{H}$ 11.16 ppm is shown to have the connectivity with three singlets observed at $\delta_{H}$ 2.20, 2.19, and 2.12 ppm for CH$_3$ protons. This NH proton is assigned to H2 atom and the
Figure 2.2.11 A VT $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectra of XI shown for CH$_3$ protons.
signal at δH 5.52 ppm is assigned to H3 atom shown in Figure 2.2.13. The non-bonded distances involving H2 and H3 with three o-CH₃ protons of the xylol moiety of the guanidine in XI is listed in Table 2.2.9. The NH proton that appears at δH 5.52 ppm has connectivity with CH₃ protons that appear at δH 1.67 ppm. Thus, the signals at δ 1.65, 2.41 (CH₃), and 5.42, 11.14 (NH) ppm are assigned to trans anti anti isomer. The signals at δH 1.80, 1.85, 1.92, 1.94, 1.97, and 2.04 ppm cannot be assigned to a particular conformer as these protons did not show any reasonable connectivity with NH protons.

Table 2.2.9 Non-bonded H···H contacts (Å) between NH protons and CH₃ protons in XI

<table>
<thead>
<tr>
<th></th>
<th>H2···H16C</th>
<th>H3···H24B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H2···H16C</td>
<td>2.318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2···H8A</td>
<td>2.757</td>
<td></td>
<td>2.506</td>
</tr>
<tr>
<td>H2···H24A</td>
<td>3.210</td>
<td></td>
<td>5.180</td>
</tr>
<tr>
<td>H3···H8A</td>
<td></td>
<td>3.389</td>
<td></td>
</tr>
<tr>
<td>H3···H16B</td>
<td></td>
<td></td>
<td>5.180</td>
</tr>
</tbody>
</table>

2.2.3.3 Palladium(IV) Guanidine Oxo Adduct

2.2.3.3.1 Synthesis

Pd(OC(O)CF₃)₂ was treated with LH₂²⁺ in 1:2 mole ratio in toluene under reflux condition for 12 h to afford trans-[(CF₃(O)CO)₂Pd(O)(ArN=C(N(H)Ar)₂)₂] as orange crystals in 95% yield as illustrated in Scheme 2.2.5. The adduct XIII was crystallized from toluene/CHCl₃ mixture at ambient temperature over a period of several days.
Figure 2.2.12 A two-dimensional NOESY NMR (400MHz, CD$_2$Cl$_2$) spectrum of XI measured at 243 K.
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Figure 2.2.13 Expansion of the 2D NOESY NMR (400 MHz, CD$_2$Cl$_2$) spectrum of XI measured at 243 K in the 5.20–7.60 ppm range versus 1.50–2.70 ppm range.

Figure 2.2.14 Expansion of the 2D NOESY NMR (400 MHz, CD$_2$Cl$_2$) spectrum of XI measured at 243 K in the 10.70–11.70 ppm range versus 1.50–2.70 ppm range.
The molecular structure of XIII was determined by single crystal X-ray diffraction data at 120, 150, and 273 K. Selected bond distances and bond angles are listed in Table 2.2.10 and 2.2.11, respectively. The structural parameters of XIII are discussed only for 120 K data set as the parameters obtained from 150 and 273 K data sets are identical to that obtained at 120 K. The molecular structure of XIII illustrated in Figure 2.2.15.

**Scheme 2.2.5** Synthesis of Palladium(IV) Guanidine Oxo Adduct XIII.

![Scheme 2.2.5](image)

### 2.2.3.3.2 Solid State Structural Aspects

The structure of XIII was initially solved in monoclinic Cc space group with a reasonable R factor (~ 6.0%). However, the refinement never converged. Further, check.cif IUCr validation suggested a centrosymmetric $C2/c$ space group. Hence, the structure was solved in $C2/c$ space group satisfactorily with acceptable bond parameters and R factor. The palladium atom in XIII is surrounded by oxygen atom of two monodentate trifluoroacetate moiety in the mutual trans position as are the imine nitrogen atom of two guanidines. The fifth coordination site is occupied by an oxo oxygen atom. Thus, the geometry of the palladium atom can be described as a square pyramidal. The palladium atom and the oxo oxygen and toluene were shown to lie on a crystallographic two fold symmetry and thus two halves of the molecule is related by $C_2$ symmetry. It would be of interest to consider another structural possibility for XIII. i.e. Pd(II) aquo guanidine species, [(CF$_3$C(O)O)$_2$Pd(H$_2$O)(ArN=C(NHAr)$_2$)$_2$]. Our attempts to locate the hydrogen atoms near the oxygen atom on the apical position of palladium were not successful and
refinement did not converge and hence the possibility of Pd(II) aquo guanidine species for XIII is ruled out.

Table 2.2.10 Selected Bond Distances (Å) for the Adduct XIII Measured at 120, 150 and 273 K.

<table>
<thead>
<tr>
<th></th>
<th>120 K</th>
<th>150 K</th>
<th>273 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(1)-O(3)</td>
<td>1.865(8)</td>
<td>1.878(6)</td>
<td>1.860(2)</td>
</tr>
<tr>
<td>Pd(1)-O(1)</td>
<td>2.020(3)</td>
<td>2.015(3)</td>
<td>2.021(3)</td>
</tr>
<tr>
<td>Pd(1)-N(1)</td>
<td>2.041(3)</td>
<td>2.041(3)</td>
<td>2.046(3)</td>
</tr>
<tr>
<td>O(1)-C(26)</td>
<td>1.254(5)</td>
<td>1.258(5)</td>
<td>1.253(5)</td>
</tr>
<tr>
<td>O(2)-C(26)</td>
<td>1.218(5)</td>
<td>1.219(5)</td>
<td>1.205(5)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.310(5)</td>
<td>1.311(5)</td>
<td>1.309(4)</td>
</tr>
<tr>
<td>N(1)-C(2)</td>
<td>1.426(5)</td>
<td>1.425(5)</td>
<td>1.425(4)</td>
</tr>
<tr>
<td>N(2)-C(1)</td>
<td>1.366(5)</td>
<td>1.372(5)</td>
<td>1.366(5)</td>
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<tr>
<td>N(2)-C(10)</td>
<td>1.413(5)</td>
<td>1.417(5)</td>
<td>1.421(5)</td>
</tr>
<tr>
<td>N(3)-C(1)</td>
<td>1.357(5)</td>
<td>1.352(5)</td>
<td>1.349(5)</td>
</tr>
<tr>
<td>N(3)-C(18)</td>
<td>1.455(5)</td>
<td>1.460(6)</td>
<td>1.451(5)</td>
</tr>
</tbody>
</table>

Table 2.2.11 Selected Bond Angles (deg.) for the Adduct XIII Measured at 120, 150 and 273 K.

<table>
<thead>
<tr>
<th></th>
<th>120 K</th>
<th>150 K</th>
<th>273 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(3)-Pd(1)-O(1)</td>
<td>92.9(8)</td>
<td>93.2(8)</td>
<td>92.8(8)</td>
</tr>
<tr>
<td>O(1)-Pd(1)-O(1)'</td>
<td>174.2(2)</td>
<td>173.7(2)</td>
<td>174.4(2)</td>
</tr>
<tr>
<td>O(1)-Pd(1)-N(1)'</td>
<td>92.4(1)</td>
<td>92.7(1)</td>
<td>92.8(1)</td>
</tr>
<tr>
<td>O(3)-Pd(1)-N(1)</td>
<td>88.5 (8)</td>
<td>88.7(9)</td>
<td>88.6(8)</td>
</tr>
<tr>
<td>O(1)-Pd(1)-N(1)</td>
<td>87.7 (1)</td>
<td>87.5(1)</td>
<td>87.4(1)</td>
</tr>
<tr>
<td>N(1)'-Pd(1)-N(1)</td>
<td>177.1(2)</td>
<td>177.3 (2)</td>
<td>177.2(2)</td>
</tr>
<tr>
<td>C(26)-O(1)-Pd(1)</td>
<td>120.1(2)</td>
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<td>120.2(3)</td>
</tr>
<tr>
<td>C(1)-N(1)-C(2)</td>
<td>119.5(3)</td>
<td>119.6(3)</td>
<td>119.2(3)</td>
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<tr>
<td>C(1)-N(1)-Pd(1)</td>
<td>118.7(2)</td>
<td>118.7(3)</td>
<td>119.0(2)</td>
</tr>
<tr>
<td>C(2)-N(1)-Pd(1)</td>
<td>120.9(2)</td>
<td>120.9(3)</td>
<td>120.9(2)</td>
</tr>
<tr>
<td>C(1)-N(2)-C(10)</td>
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<td>124.3(3)</td>
<td>124.6(3)</td>
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<td>123.3(4)</td>
<td>124.4(3)</td>
</tr>
<tr>
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<td>123.3(3)</td>
<td>124.0(4)</td>
<td>123.3(3)</td>
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<tr>
<td>N(1)-C(1)-N(2)</td>
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<td>118.8(3)</td>
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<tr>
<td>N(3)-C(1)-N(2)</td>
<td>117.8(3)</td>
<td>117.3(4)</td>
<td>117.9(3)</td>
</tr>
</tbody>
</table>

The stereochemistry around the guanidine unit in XIII is same as that observed in IX, i.e. trans syn anti-anti. The angle between the plane of the CN_3 unit and the square plane around the palladium atom is 88.63(13)°. The values of Δ_CN: 0.055(6) Å and Δ_CN': 0.045(6) Å are smaller than those observed for LH_2^{2,5-sybyl} (Δ_CN: 0.098(3) Å and Δ_CN': 0.094(3) Å).
Chapter 2: Results and Discussion

0.096(3) Å. The ρ 0.96 value is slightly greater than that observed for LH$_2^{2,5}$-syl (ρ: 0.93).

The amino nitrogens are planar. These structural features suggest that n−π conjugation is greater in XIII as compared with LH$_2^{2,5}$-syl. The Pd−O: 1.865(8) Å distance is shorter than the sum of the covalent radii of Pd(II) and oxygen, 2.07 Å \(r\text{(Pd(II))}: 1.39 \text{ Å}; \ r\text{(O)}: 0.68 \text{ Å}. \)\(^{15}\) Further, the Pd−O: 1.865(8) Å distance in XIII is significantly shorter than the Pd−OH$_2$: 2.064(3)−2.276(3) Å distance reported for the neutral palladium aquo complexes.\(^{20}\) Thus, the adduct XIII is shown to be palladium(IV) oxo species rather than palladium(II) aquo species. The longer Pd=O distance in XIII as compared with the only known Pd(IV)=O complex (1.60(2) Å)\(^{21}\) could be due to the involvement of the oxo oxygen in the former complex in intramolecular N−H···O hydrogen bonding (see below). One of the NH protons was shown to act as a bifurcated hydrogen bond donor and thus participates in intramolecular N−H···O hydrogen bonding. Additionally, an intramolecular C−H···F hydrogen bonding was observed between fluorine atom of CF$_3$ moiety and one of the CH$_3$ protons of =NAr unit as illustrated in Figure S2.2.6.

2.2.3.3.3 Spectroscopic Data

The IR spectrum of the adduct XIII revealed two bands at 3381 and 3244 cm$^{-1}$ assignable to two distinct NH moieties. Further, an intense band was observed at 1604 cm$^{-1}$ assignable to the C=NH moiety. The \(\Delta \nu = 1604 − 1654 = −50 \text{ cm}^{-1}\) value indicates coordination of the guanidine unit to the palladium atom through the imine nitrogen. The TFA moiety revealed two bands at 1702 and 1451 cm$^{-1}$ assignable to \(\nu_a\text{(OCO)}\) and \(\nu_s\text{(OCO)}\), respectively. The CF$_3$ moiety revealed two bands at 1188 and 1146 cm$^{-1}$ assignable to the C−F stretch. The $^1$H NMR spectrum of XIII revealed six singlets at \(\delta_H\) 1.58, 1.83, 2.06, 2.10, 2.15 and 2.23 ppm assignable to CH$_3$ protons of the guanidine. Two NH protons revealed two singlets at \(\delta_H\) 5.53 and 9.61 ppm. The $^{13}$C NMR spectrum of XIII revealed five singlets at \(\delta_C\) 16.7, 17.2, 17.4, 20.5, and 20.8 ppm instead of anticipated six singlets due to overlap of two signals. A quartet was observed at \(\delta_C\) 114.2 ppm \(\left(\nu_{\text{CF}} = 290.3 \text{ Hz}\right)\) and a broad multiplet was observed at \(\delta_C\) 163.3 (br) assignable to CF$_3$ and OC(O) carbon, respectively.
Figure 2.2.15 The ORTEP representation of XIII at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
2.2.3.3.4 Oxo Transfer Reaction

To confirm the presence of oxo species in XIII, an NMR scale competition experiment was carried out as described below. The reaction of XIII with PTA in acetonitrile-$d_3$ at 40 °C afforded a dark brown solution (see Scheme 2.2.6). The $^{31}$P{¹H} NMR spectrum of the solution revealed three peaks at $\delta_P$ -13.4 (major), -40.7 (minor) and -50.4 (br, minor) ppm as illustrated in Figure 2.2.16 and this spectral pattern suggests the presence of O=PTA and two other minor unknown products in solution. However, three signature doublets observed at $\delta_H$ 3.67, 4.00, and 4.17 ppm in about 6:3:3 ratios with $J_{HP} = 9.5, 13.2$ and $14.4$ Hz, respectively matches well with CH$_2$ protons of O=PTA measured in CD$_3$CN (see Experimental Section). The results of oxo transfer reaction thus complement the X-ray diffraction data and thus support the presence of oxo species in XIII rather than water. This type of experiment was shown to serve as an evidence for the presence of L$_n$M=O unit. Only one Pd(IV) oxo compound is known in the literature. There is a great deal of controversy in the literature concerning the existence of Pt(IV) and Pd(IV) oxo species. The existence of Pt(IV) oxo species has been proven beyond the doubt. Factors that stabilize late transition metal oxo species particularly, L$_n$Pt(IV)=O and Pd(IV)=O has been discussed at length.

One of the reasons for the stabilization of Pd(IV) in XIII could be attributed to the presence of more electronegative TFA moiety. It has been shown in the literature that the electronegative substituents stabilize Pd(IV) compounds. Palladium(IV) oxo species has been suggested as transient intermediate in several organic transformations.

Scheme 2.2.6 Oxo-transfer Reaction
Figure 2.2.16 The $^{31}$P/$^1$H NMR (CD$_3$CN, 161.8 MHz) spectrum of the reaction on mixture obtained from XIII and PTA shown in the region between – 200.0 to + 200.0 ppm.
2.2.4 Catalytic Studies

The cross coupling reactions of aryl chlorides are more challenging than its bromo and iodo analogues.\textsuperscript{28,29} The catalytic efficacy of adducts IX–XIII was tested in Heck coupling reaction involving one equivalent of chlorobenzene and 1.5 equivalent of methylacrylate in the presence of 1.5 equiv of Et\textsubscript{3}N as a base in DMF at 90 °C as shown in Scheme 2.2.7. The mol% of the precatalyst was fixed at 0.1, 0.01 and 0.001 with respect to chlorobenzene. The yield of trans methylcinnamate obtained with different

Scheme 2.2.7 Catalysis Reaction

\[
\text{Scheme 2.2.7 Catalysis Reaction}
\]

\[
\text{Cl} + \underbrace{\text{C} = \text{C}}_{\text{trans-[X} \text{Pd(E)(LH}^2_{2,5} \text{-} \text{X} \text{My}]}_{\text{catalyst}} \rightarrow \text{Methylcinnamate}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst (mol%)</th>
<th>Yield(^b) (%)</th>
<th>TON(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>0.1</td>
<td>81</td>
<td>813</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>80</td>
<td>8049</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>74</td>
<td>74630</td>
</tr>
<tr>
<td>X</td>
<td>0.1</td>
<td>82</td>
<td>826</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>81</td>
<td>8107</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>78</td>
<td>78000</td>
</tr>
<tr>
<td>XI</td>
<td>0.1</td>
<td>80</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>78</td>
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<td>0.001</td>
<td>76</td>
<td>76300</td>
</tr>
<tr>
<td>XII</td>
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<tr>
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<td>83</td>
<td>8314</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>81</td>
<td>81100</td>
</tr>
<tr>
<td>XIII</td>
<td>0.1</td>
<td>91</td>
<td>913</td>
</tr>
<tr>
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<td>0.01</td>
<td>90</td>
<td>9036</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>89</td>
<td>89130</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: Chlorobenzene (1.0 mmol), methylacrylate (1.5 mmol), Et\textsubscript{3}N (1.5 mmol) in DMF (5 mL). \(^b\)Purity of the product was checked by \(^1\)H NMR data; Isolated yields of the products are based on chlorobenzene from the average of two runs. \(^c\)TON = mole of product/mole of catalyst.
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mol % of precatalysts is listed in Table 2.2.11. The results indicated that adducts IX and XII are highly active whereas the adduct XIII is the most active catalyst for coupling reaction. The yield and TON are greater for XIII than those observed for IX–XII.

2.2.5 CONCLUSION
Cyclometalation resistant LH$_2^{2,5}$-xylyl was isolated and characterized by IR, NMR ($^1$H and $^{13}$C) and X-ray diffraction data. The observed conformations of adducts IX–XI in the solid state appear to arise from the minimization of steric factor and maximization of noncovalent interactions while that in XII appear to be controlled mainly by steric factor. Adducts IX and XI revealed a restricted C–N(H)Ar single bond rotation in solution and thus present as a mixture of two conformers as revealed by a VT $^1$H NMR data. A remarkable Pd(IV) oxo species was isolated for the first time and structurally characterized. Adducts, IX–XIII were shown to be effective precatalysts for Heck coupling reaction of chlorobenzene and methylacrylate.
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2.2.6 REFERENCES


Chapter 2: Results and Discussion


Chapter 2: Results and Discussion

Influence of Conformations of \textit{sym} \textit{N,N',N''-}Triarylguanidines on Their Reactivity Towards \textit{cis-}[Cl}_2Pt(S(O)Me)_2]:

Cyclometalation Versus Substitution

2.3.1 ABSTRACT

The reaction of \textit{cis-}[Cl}_2Pt(S(O)Me)_2] with one equiv of \textit{sym} \textit{N,N',N''-}triarylguanidines, ArN=C(NHAr) (Ar = 2-MeC_6H_4 (LH^2-2-tolyl), 2-(MeO)C_6H_4 (LH^2-2-anisyl), 4-MeC_6H_4 (LH^2-4-tolyl), 2,5-Me_2C_6H_3 (LH^2-2,5-xylyl), and 2,6-Me_2C_6H_3 (LH^2-2,6-xylyl)) carried out separately in toluene under reflux condition for 3 h afforded 1:1 adducts [Cl}_2Pt(S(O)Me)(ArN=C(NHAr)] (ArN=C(NHAr): LH^2-2-tolyl (XIV), LH^2-2-anisyl (XV), LH^2-4-tolyl (XVI), LH^2-2,5-xylyl (XVII), and LH^2-2,6-xylyl (XVIII)) in 83–99% yield. The reaction of \textit{cis-}[Cl}_2Pt(S(O)Me)_2] with one equiv of LH^2-2-anisyl in the presence of one equivalent of NaOAc in methanol under reflux condition for 3 h afforded six-membered \[\text{[C},\text{N}\] platinacycle, \[\text{Pd}\{\kappa^2(C,N)-C_6H_3(OMe)-3(NHC(NHAr)(=NAr))-2\}\text{Cl}(S(O)Me)_2]\] (Ar = 2-(MeO)C_6H_4; XX) in 93% yield and the same reaction carried out with bulkier LH^2-2-tolyl and LH^2-2,5-xylyl for 12 h afforded six-membered \[\text{[C},\text{N}\] platinacycles, \[\text{Pd}\{\kappa^2(C,N)-C_6H_3Me_x-z(NHC(NHAr)(=NAr))-2\}\text{Cl}(S(O)Me)_2]\] (x = 3, y = 1, z = 3; Ar = 2-MeC_6H_4 (XXI); x = 2, y = 2, z = 3,6; Ar = 2,5-Me_2C_6H_3 (XXII)) in 92 and 89% yield, respectively. The reaction of \textit{cis-}[Cl}_2Pt(S(O)Me)_2] with one equiv of LH^2-2-tolyl and LH^2-4-tolyl carried out separately in the presence of one equivalent of NaOAc in methanol under reflux condition for 3 h afforded acetate substitution products, \textit{trans-}[(AcO)ClPt(S(O)Me)_2](L)) (L = LH^2-2-tolyl (XXIII), L = LH^2-4-tolyl (XXIV)) in 93% yield. The new compounds were characterized by IR, NMR (\textit{\textit{1}}H, \textit{13}C, and \textit{195}Pt), microanalytical and mass spectral data. The platinum atom in adducts XIV, XVII, and XVIII was shown to exhibit a \textit{trans} configuration whereas that in XV and XXIII was shown to exhibit a \textit{cis} configuration. The sulfur atom of Me_2S(O) was shown to coordinate to the platinum atom in XX in \textit{cis} relation with respect to the aryl carbon. Compound XXIII represents the first structurally characterized acetate substitution product in the cyclometalation reaction mediated by external base, NaOAc. Factors responsible for the observance of cyclometalation products (XX–XXII) versus substitution products (XXIII)
and XXIV) and the overall mechanism of C–H activation process were discussed in light of the conformations, and steric/electronic properties of the guanidines.

2.3.2 INTRODUCTION

Platinum(II) imine complexes are one of the interesting classes of coordination compounds due to their relevance as precursors for [C,N] platinacycles and as scaffolds for stoichiometric C–H and C–C activation process.\textsuperscript{1–12} Further, these complexes have been shown to exhibit interesting antitumor activity,\textsuperscript{13–15} materials properties such as mesomorphism, and liquid crystalline property,\textsuperscript{16} photophysical\textsuperscript{17,18} and catalytic properties.\textsuperscript{19} Platinum(II) guanidine complexes are sparse in the literature up until 2002 and the first crystallographically characterised platinum(II) guanidine complex was reported by N. M. Kostic and coworkers only in 1990.\textsuperscript{20–22} Guanidines in these complexes were unsubstituted, and monosubstituted in their neutral, and monoanionic forms exhibiting monodentate and bridging bidentate coordination modes. Sym N,N',N″ trisubstituted guanidines, RN=C(NHR)\textsubscript{2} (R = alkyl/aryl) are both sterically and electronically flexible N-donor ligands in that the donor characteristics and coordination modes can be modulated by systematically changing the R substituent. Further, this class of guanidines can be mono and di-deprotonated to afford guanidinate(1–) monoanion, A and guanidinate (2–) dianion B as illustrated in Scheme 1.1.4 in Chapter 1. This class of guanidines was shown to exhibit monodentate coordination mode in their neutral form, bridging bidentate, and chelating bidentate coordination modes in their anionic forms.\textsuperscript{23,24} Three platinum(II) complexes of N,N',N″-triphenylguanidine, PhN=C(NHPh)\textsubscript{2} (LH\textsubscript{2} Ph) are also known wherein guanidinate(1–) and guanidinate (2–) anion chelates the platinum.\textsuperscript{25,26} Platinum(II) complexes of bicyclic guanidine, hPPH (1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine) and strongly donating functionalised bis(guanidine) complexes are known and in the latter complexes the ligands were shown to bind the platinum atom in neutral monodentate and bidentate forms.\textsuperscript{27,28} The coupling reaction between platinum(II) bound nitrile with protic nucleophiles such as ammonia, primary amines, tetramethylguanidine, N,N′-diphenylguanidine, and cyanoguanidine have been studied by Kukushkin and others and these reactions have been shown to afford a new class of platinum(II) guanidine complexes.\textsuperscript{29}
Recently, we have reported \( \text{sym} \ N,N',N''\text{-tris}(2\text{-anisyl})\text{guanidine}, \text{ArN=C(NHAr)}_2 \) \((R = 2-(\text{MeO})\text{C}_6\text{H}_4)\) derived six-membered \([C,N]\) palladacycles of the types, \([\text{(C,N)}\text{Pd(µ-X)}]_2\), \([\text{(C,N)}\text{PdXL}]\) \((X = \text{OC(O)R; Br})\) and a novel ring contracted five-membered \([C,N]\) palladacycle, \([\text{(C,N)}\text{PdBr(C≡NXy)}]\), their structural aspects and solution behaviour of some representative palladacycles.\(^{30}\) In continuation of our interests in exploring the coordination chemistry aspects of \( \text{sym} \ N,N',N''\text{-trisubstituted guanidines} \) towards platinum group metals, we report herein the facile and high yield \((≥ 89\%)\) synthesis of three classes of platinum(II) guanidine complexes namely, \([\text{Cl}_2\text{Pt(S(O)Me}_2)](\text{ArN=C(NHAr)}_2)\) \((\text{Ar} = 2-\text{MeC}_6\text{H}_4) \text{ (XIV)}, 2-(\text{MeO})\text{C}_6\text{H}_4 \text{ (XV}), 4-\text{MeC}_6\text{H}_4 \text{ (XVI)}, 2,5-\text{Me}_2\text{C}_6\text{H}_3 \text{ (XVII)}, \) and \(2,6-\text{Me}_2\text{C}_6\text{H}_3 \text{ (XVIII)})\), six-membered \([C,N]\) platinacycles, \([\text{Pd{κ}_2(C,N)-C}_6\text{H}_{x-y}(\text{NH}\text{C(NHAr)}(=\text{NAr}))_2\text{Br(S(O)Me}_2)]\) \((R = \text{OMe}; x = 3; y = 1; z = 3; \text{Ar} = 2-(\text{MeO})\text{C}_6\text{H}_4 \text{ (XX)}, \text{R} = \text{Me}, x = 3, y = 1, z = 3; \text{Ar} = 2-\text{MeC}_6\text{H}_4 \text{ (XXI)}, \text{R} = \text{Me}; x = 2, y = 2, z = 3,6; \text{Ar} = 2,5-\text{Me}_2\text{C}_6\text{H}_3 \text{ (XXII)}) and acetate substitution products, \(\text{cis-}[\text{(AcO)}\text{ClPt(S(O)Me}_2)](\text{ArN=C(NHAr)}_2)\) \((\text{Ar} = 2-\text{MeC}_6\text{H}_4 \text{ (XXIII)} \) and \(4-\text{MeC}_6\text{H}_4 \text{ (XXIV)})\) and the line drawing pictures of these complexes are collected in Chart 2.3.1. The influence of steric/electronic properties and conformations of \( \text{sym} \ N,N',N''\text{-triaryl guanidines}, \text{ArN=C(NHAr)}_2 \) \((\text{Ar} = 2\text{-tolyl, 2-anisyl, 4-tolyl, 2,5-xylyl, and 2,6-xylyl})\) upon the nature of products and a plausible mechanism of formation of six-membered \([C,N]\) platinacycles, \text{XX} and \text{XXI} are also discussed. The results presented in this paper have been communicated in a international conference.\(^{31}\)

2.3.3 RESULTS AND DISCUSSION

2.3.3.1 Platinum(II) Guanidine Adducts

2.3.3.1.1 Synthesis

The reaction of \( \text{cis-}[\text{Cl}_2\text{Pt(S(O)Me}_2)] \) with one equiv of \( \text{LH}_2^{2\text{-tolyl}}, \text{LH}_2^{2\text{-anisyl}}, \text{LH}_2^{4\text{-tolyl}}, \text{LH}_2^{2,5\text{-xylyl}}, \) and \( \text{LH}_2^{2,6\text{-xylyl}} \) carried out separately in toluene under reflux condition for 3 h afforded 1:1 adducts, \text{XIV–XVIII} in 83–99\% yield. The new adducts were purified by evaporation of mother liquor at ambient condition to afford a solid and subsequent crystallization from CHCl\textsubscript{3}/toluene or CH\textsubscript{2}Cl\textsubscript{2}/toluene mixture at ambient condition in each case. The formation of 1:1 adducts are illustrated in Scheme 2.3.1.
Adducts XIV–XVII were obtained as pale yellow crystals while the adduct XVIII was obtained as light brown crystals. Adducts XIV–XVIII are soluble in chloroform, dichloromethane, but sparingly soluble in acetone, methanol, and toluene. On one occasion, the reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with LH₂²-tolyt in toluene under reflux condition for 3 h afforded [LH₃²-tolyt][PtCl₃] (XIX) as a minor product. The salt XIX was characterized by only single crystal X-ray diffraction data as the sample quantity was not sufficient for other data.

**Scheme 2.3.1 Synthesis of Adducts XIV–XVIII**

<table>
<thead>
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<th>LH₂²-tolyt</th>
<th>Ar</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH₂²-aryl</td>
<td>2-MeC₆H₄</td>
<td>XIV 96</td>
</tr>
<tr>
<td>LH₂²-anisyl</td>
<td>2-(MeO)C₆H₄</td>
<td>XV 83</td>
</tr>
<tr>
<td>LH₂²-tolyl</td>
<td>4-MeC₆H₄</td>
<td>XVI 99</td>
</tr>
<tr>
<td>LH₂²,5-xylty</td>
<td>2,5-Me₂C₆H₃</td>
<td>XVII 94</td>
</tr>
<tr>
<td>LH₂²,6-xylty</td>
<td>2,6-Me₂C₆H₃</td>
<td>XVIII 92</td>
</tr>
</tbody>
</table>
2.3.3.1.2 Single Crystal X-ray Diffraction Data

Adducts XIV, XV, XVII and XVIII were characterized by single crystal X-ray diffraction data. Adducts XIV and XVII were shown to possess no solvent molecule in the crystal lattice while XV and XVIII were obtained as \((XV)_{2} \cdot 3\text{CHCl}_{3}\), and \((XVIII)_{2} \cdot \text{toluene}\), respectively. The molecular structures of XIV, XV, XVII, and XVIII are depicted in Figures 2.3.1–2.3.4, respectively. Two molecules were observed in an asymmetric unit in the case of XV and XVIII. Selected bond distances and bond angles are listed in Tables 2.3.1–2.3.4, respectively. The platinum atom in adducts XIV, XV, XVII, and XVIII is surrounded by two chloride, an imine nitrogen of the guanidine, and sulfur atom of DMSO and displayed a slightly distorted square planar geometry. Two chlorides are located trans to each other around the platinum atom as are DMSO and the guanidine in XIV, XVII, and XVIII while the aforementioned pairs of substituents are located cis to each other in XV.

![An ORTEP representation of XIV at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.](image)

Figure 2.3.1 An ORTEP representation of XIV at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Chapter 2: Results and Discussion

Figure 2.3.2 An ORTEP representation of XV [molecule 1 (left) and molecule 2 (right)] at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Figure 2.3.3 An ORTEP representation of XVII at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Figure 2.3.4 An ORTEP representation of XVIII [(molecule 1 (left) and molecule 2 (right))] at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Chapter 2: Results and Discussion

**Table 2.3.1** Selected Bond Distances (Å) and Bond Angles (deg.) for 1:1 Adduct XIV.

<table>
<thead>
<tr>
<th>Bond Distances (Å) and Bond Angles (deg.)</th>
<th>XIV</th>
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<tr>
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</tr>
<tr>
<td>Pt1-Cl2</td>
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</tr>
<tr>
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<td>Pt1-N1</td>
<td>2.060(3)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.329(1)</td>
</tr>
<tr>
<td>N2-C1</td>
<td>1.374(1)</td>
</tr>
<tr>
<td>N3-C1</td>
<td>1.330(1)</td>
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<tr>
<td>Pt1-N1</td>
<td>1.374(1)</td>
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<tr>
<td>N1-C1</td>
<td>1.401(1)</td>
</tr>
<tr>
<td>N2-C9</td>
<td>1.435(1)</td>
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<tr>
<td>N3-C16</td>
<td>1.423(1)</td>
</tr>
<tr>
<td>S1-O1</td>
<td>1.468(8)</td>
</tr>
</tbody>
</table>

**Table 2.3.2** Selected Bond Distances (Å) and Bond Angles (deg.) for 1:1 Adduct XV.

<table>
<thead>
<tr>
<th>Bond Distances (Å) and Bond Angles (deg.)</th>
<th>XV</th>
</tr>
</thead>
<tbody>
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<td>C1-N3-C16</td>
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<tr>
<td>S2-Pt2-S2</td>
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<td>C25-N6-Pt2</td>
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Table 2.3.3 Selected Bond Distances (Å) and Bond Angles (deg.) for 1:1 Adduct XVII.

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<td>N3-C1</td>
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<td>N3-C18</td>
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<td>S1-O1</td>
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Table 2.3.4 Selected Bond Distances (Å) and Bond Angles (deg.) for 1:1 Adduct XVIII.

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<td>Pt1-C12</td>
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<td>Pt2-C14</td>
<td>2.328(9)</td>
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<tr>
<td>Pt1-S1</td>
<td>2.232(7)</td>
<td>Pt2-S2</td>
<td>2.215(9)</td>
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<td>Pt2-N4</td>
<td>2.132(2)</td>
<td>N1-Pt1-C1</td>
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<td>N1-C1</td>
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<td>N4-C28</td>
<td>1.296(4)</td>
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<td>N2-C1</td>
<td>1.449(4)</td>
<td>N5-C28</td>
<td>1.358(4)</td>
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<tr>
<td>N3-C1</td>
<td>1.388(3)</td>
<td>N5-C28</td>
<td>1.345(4)</td>
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<td>N1-C2</td>
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<td>N4-C29</td>
<td>1.441(3)</td>
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<td>1.465(4)</td>
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Chapter 2: Results and Discussion

The bond parameters around the platinum atom in XIV, XVII, and XVIII (molecule 1) are typical for the 1:1 adduct of the type trans-[ClPt(S(O)Me₂)L] (L = Nitrogen donor ligand with imine and oxime functionality) reported in the literature.²⁻⁴,⁶⁻⁸,¹¹⁻¹₈ The Pt−N distance in XIV (2.060(3) Å), XVII (2.044(2) Å) and XVIII (2.038(2) Å, molecule 1) is slightly shorter than that observed in XVIII (2.132(2) Å; molecule 2) and the predicted value of 2.06 Å for a Pt−N single bond distance (covalent radius of Pt(II)): 1.36 Å; covalent radius of r(N(sp²)): 0.71 Å).³² This could be ascribed to subtle packing forces in the crystal lattice (see below). In adducts XIV, XV, XVII and XVIII, the Pt−S distances vary from 2.203(1) to 2.232(7) Å, which is in good agreement with the mean Pt-S distance, 2.216 Å for S-coordinated sulfoxides.³³ The S=O distance, 1.432(3) Å in molecule 1 is shorter than that observed in molecule 2 (1.489(3) Å of XVIII, XIV (1.468(8) Å), XV (1.468(3) (molecule 1); 1.467(3) (molecule 1) Å), and XVII (1.472(2) Å).

The conformation of the guanidine unit in XIV, XV, and XVII is anti-anti ααβ and that in XVIII is anti-anti while the conformation of LH₂²-tolyl and LH₂²,5-xylyl is anti-anti αβα and that of LH₂²-anisyl is syn-anti αββ and that of LH₂²,6-xylyl is syn-anti.³⁴ The difference in the conformation of the guanidine in XV and XVIII as compared with LH₂²-anisyl and LH₂²,6-xylyl may be ascribed to the steric relief upon coordination to the platinum atom in the former complexes. The structure and bonding of the CN₃ core of the guanidine in XIV, XV, XVII, and XVIII can be understood from the values of ΔCN, ΔCN′,³⁵ and ρ³⁶ parameters which are defined and listed in Table 2.3.5. ΔCN, ΔCN′ values in XIV, XV, XVII, and XVIII are smaller than the corresponding values known for the respective guanidine in accord with the expected increase in the n−π conjugation involving the NHAr lone pair with C=N π* orbital upon coordination to the platinum atom. Further, ΔCN value is slightly greater than ΔCN′ value in XIV and XVIII but the difference between the values of these parameters are comparable in XV and identical in XVII. The ρ value in XIV, XV, XVII, and XVIII is slightly greater or greater than that known for the respective uncoordinated guanidine indicating a greater n−π conjugation in 1:1 adducts. Both amino nitrogens are planar in the 1:1 adducts. Adducts XIV, XV, XVII
and XVIII are shown to possess numerous noncovalent interactions in the crystals lattice as illustrated in Figures S2.3.1–S2.3.9.

**Table 2.3.5**  \( \Delta_{CN}, \Delta_{CN}' \) (Å), and \( \rho \) parameters for Adducts XIV, XV, XVII, XVIII and Guanidines.

\[
\begin{array}{cccc}
\text{Adduct} & \Delta_{CN} (\text{Å}) & \Delta_{CN}' (\text{Å}) & \rho \\
\hline
\text{XIV} & 0.045(2) & 0.001(2) & 0.98 \\
\text{LH}_2^{2\text{-tolyl}} & 0.095(6) & 0.098(6) & 0.93 \\
\text{XV} & 0.044(5) & 0.032(5) & 0.97 \\
\text{LH}_2^{2\text{-anisyl}} & 0.100(6) & 0.98(6) & 0.92 \\
\text{XVII} & 0.042(4) & 0.042(4) & 0.97 \\
\text{LH}_2^{2,6\text{-xylyl}} & 0.096(2) & 0.098(2) & 0.93 \\
\text{XVIII} & 0.111(6) & 0.050(5) & 0.94 \\
\text{LH}_2^{2,6\text{-xylyl}} & 0.062(6) & 0.049(6) & 0.96 \\
\end{array}
\]

The molecular structure of the salt XIX is shown in Figure 2.3.5. Selected bond distances and bond angles are listed in Table 2.3.6. The guanidinium cation, \( [\text{C(NHAr)}_3]^+ \) is connected to the \( [\text{PtCl}_3(\text{S(O)Me}_2)]^- \) anion via a pair of charge assisted N–H···Cl hydrogen bonding. The platinum atom is surrounded by three chloro ligand and the sulfur atom of \( \text{S(O)Me}_2 \). The platinum atom exhibits a square planar geometry. All nitrogen atoms are planar.
Figure 2.3.5 An ORTEP representation of the salt XIX at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
Table 2.3.6 Selected Bond Distances (Å) and Bond Angles (deg.) for Platinum(II) Salt XIX.

<table>
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<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (deg)</th>
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<td>2.2919(2)</td>
<td>88.89(5)</td>
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<tr>
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<td>2.3205(2)</td>
<td>75.97(4)</td>
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<td>90.15(5)</td>
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<td>Pt1-S1</td>
<td>2.1981(2)</td>
<td>88.57(4)</td>
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<td>1.335(6)</td>
<td>92.35(4)</td>
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<td>1.328(6)</td>
<td>125.6(4)</td>
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<td>N1-C2</td>
<td>1.432(6)</td>
<td>129.8(4)</td>
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<td>N2-C9</td>
<td>1.433(6)</td>
<td>126.2(4)</td>
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<td>N3-C16</td>
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<td>118.1(4)</td>
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<td>S1-O1</td>
<td>1.477(3)</td>
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2.3.3.1.3 IR Studies

The IR spectral data of adducts XIV–XVIII are listed in Table 2.3.7. The guanidine moiety in XIV–XVIII revealed two types of bands for the NH moieties and one band for the C=N moiety. The value of \( \nu(C=N) \) of XIV–XVIII are smaller than the value known for the respective uncoordinated guanidine.\(^{34}\) This trend suggests that the guanidine moiety in adducts XIV–XVIII is coordinated to the platinum atom through the imine nitrogen. The DMSO in XIV–XVIII revealed one band in the interval 1116–1157 cm\(^{-1}\) as anticipated for sulfur coordination.\(^{33}\)

Table 2.3.7 Selected FT-IR Data for Adducts XIV–XVIII (KBr, cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Adduct</th>
<th>( \nu(\text{NH}) )</th>
<th>( \nu(\text{C=N}) )</th>
<th>( \Delta \nu )</th>
<th>( \nu(\text{S=O}) )</th>
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<tr>
<td>XIV</td>
<td>3462, 3377</td>
<td>1620</td>
<td>−38</td>
<td>1142</td>
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<tr>
<td>XV</td>
<td>3449, 3337</td>
<td>1615</td>
<td>−40</td>
<td>1116</td>
</tr>
<tr>
<td>XVI</td>
<td>3471, 3402</td>
<td>1619</td>
<td>−26</td>
<td>1129</td>
</tr>
<tr>
<td>XVII</td>
<td>3447, 3374</td>
<td>1602</td>
<td>−52</td>
<td>1139</td>
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<tr>
<td>XVIII</td>
<td>3442, 3341</td>
<td>1618</td>
<td>−21</td>
<td>1157</td>
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</table>

\(^{\text{a}}\) \( \Delta \nu = \nu(\text{C=N})_{\text{adduct}} - \nu(\text{C=N})_{\text{guanidine}} \)

2.3.3.1.4 ESI-MS Studies

Adducts XIV–XVIII were subjected to ESI-MS study to obtain the information regarding the integrity and dissociative nature of these adducts in solution. The most informative peaks for each adduct are listed in Table 2.3.8. Adducts XIV–XVII revealed
peaks at m/z (intensity %): 673.9315 (37), 648.3712 (74), 662.3568 (8), and 833.9860 (12) assignable to [M]$^+$ (XIV), [M – 2HCl]$^+$ (XV), [M + Na + H – Cl]$^+$ (XVI), and [M + 3K + H]$^+$ (XVII), respectively. Adduct XVIII revealed peaks at m/z (intensity %): 776.3871 (7) and 738.2901 (8) assignable to [M + Na + K – H]$^+$ and [M + Na]$^+$, respectively. Further, adduct XVIII revealed peaks at m/z (intensity %): 1458.7161 (10), and 1395.7051 (10) assignable to [[PtCl($\mu_2$-$\kappa^1$N:$\kappa^1$N'-LH$_2$,6-xylyl)(DMSO)}$_2$ + 2K + Na]$^+$ and [[PtCl($\mu_2$-$\kappa^1$N:$\kappa^1$N'-LH$_2$,6-xylyl)(DMSO)}$_2$ + Na + 2Li]$^+$, respectively and the formation of these species are illustrated in Scheme 2.3.2.

Table 2.3.8 Selected m/z values for Adducts XIV–XVIII obtained from ESI-MS$^+$ Data. Intensity (%) is given in parenthesis.

<table>
<thead>
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<th>Adduct</th>
<th>m/z (intensity %)</th>
</tr>
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<tbody>
<tr>
<td>XIV</td>
<td>673.9315 (37), [M]$^+$; 617.9739 (12), [M + Na – S(O)Me$_2$]$^+$; 586.5962 (39), [M – 2HCl, Me]$^+$</td>
</tr>
<tr>
<td>XV</td>
<td>760.8231 (5), [M + K]$^+$; 743.9011 (7), [M + Na]$^+$; 725.0459 (8) [M + 4H]$^+$; 648.3712 (74), [M – 2HCl]$^+$</td>
</tr>
<tr>
<td>XVI</td>
<td>662.3568 (8), [M + Na + H – Cl]$^+$; 640.4659 (18) [M + 2H– Cl]$^+$; 602.6274 (20), [M – 2Cl]$^+$</td>
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<tr>
<td>XVIII</td>
<td>1458.7161 (10), [[PtCl($\mu_2$-$\kappa^1$N:$\kappa^1$N'-LH$_2$,6-xylyl)(DMSO)}$_2$ + 2K + Na]$^+$; 1395.7051 (10), [[PtCl($\mu_2$-$\kappa^1$N:$\kappa^1$N'-LH$_2$,6-xylyl)(DMSO)}$_2$ + Na + 2Li]$^+$; 776.3871 (7), [M + K + Na – H]$^+$; 738.2901 (8), [M + Na]$^+$; 680.3127 (22), [M – Cl]$^+$; 565.2996 (22), [M – 2HCl – S(O)Me$_2$]$^+$</td>
</tr>
</tbody>
</table>

Scheme 2.3.2
2.3.3.1.5 NMR Studies

The $^{195}$Pt is NMR active nucleus and the $\delta_{\text{Pt}}$ is shown to be sensitive to the coordination environment around the platinum atom, steric/electronic properties of the surrounding ligands.$^{37-39}$ Not only cis and trans isomers of $[\text{Cl}_2\text{Pt(S(O)Me}_2\text{)}\text{L}]$ ($\text{L} = N$-donor imine ligand) can be distinguished but also the E and Z configuration of the imine ligand within the adduct can be distinguished.$^{5b,8c}$ The $^{195}$Pt$\{^{1}\text{H}\}$ NMR spectrum of adducts XIV–XVIII are illustrated in Figures S2.3.10–S2.3.14, respectively. The $^{195}$Pt$\{^{1}\text{H}\}$ NMR spectrum of adducts XIV, XVII, and XVIII revealed one signal at $\delta_{\text{Pt}}$ $-2967$, $-2959$, $-2893$ ppm, respectively and these values are consistent with the values anticipated for the $^{195}$Pt nucleus surrounded by "$\text{N,Cl}_2\text{S}_{\text{DMSO}}$" set of donor atoms.$^{5b,8c,42}$ The $^{195}$Pt$\{^{1}\text{H}\}$ NMR spectrum of adduct the adduct XV revealed a closely separated pair of peaks at $\delta_{\text{Pt}}$ $-2721$ (major) and $-2771$ (minor) ppm while that of adduct XVI revealed a widely separated pair of peaks at $\delta_{\text{Pt}} = -2898$ (minor) and $-3009$ (major) ppm. It has been shown that $\delta_{\text{Pt}}$ of cis-$[\text{Cl}_2\text{Pt(S(O)R}_2\text{)}\text{L}]$ ($\text{L} = N$-donor ligand) is downfield shifted with respect to its trans counterpart and this has been ascribed to a better (d–d)$\pi$ bonding in the former.$^{5b,8c,40b,40d,40e,41a,41b}$ Hence, the major signal of XVI is assigned to trans,anti-anti isomer and the minor signal is assigned to cis,anti-anti isomer. The major signal of XV is assigned to the cis,anti-anti isomer as observed in the solid state and the minor signal is assigned to cis,syn-anti isomer but not to the trans,anti-anti isomer as $\delta_{\text{Pt}}$ would be more upfield shifted in the latter case (see Schemes 2.3.3 and 2.3.4).

Adducts XIV–XVIII were characterized by $^{1}\text{H}$ NMR data and adducts XIV and XVI–XVIII were characterized by $^{13}\text{C}$ NMR data. The $^{1}\text{H}$ NMR spectrum of XIV, XV, and XVII are illustrated in Figures 2.3.6–2.3.8 respectively. The $^{1}\text{H}$ NMR spectrum of XIV, XVI, and XVIII revealed one singlet for $\text{CH}_3$ protons of DMSO ($\delta_{\text{H}}$ $3.31$ (XIV), $3.32$ (XVI), and $3.33$ (XVIII)) and three singlets for $\text{CH}_3$ protons of the guanidine ($\delta_{\text{H}}$ $1.97$, $2.34$, $2.60$ (XIV), $2.17$, $2.22$, $2.28$ (XVI), and $2.06$, $2.33$, $2.82$ (XVIII)). On the other hand, the $^{1}\text{H}$ NMR spectrum of XVII revealed two singlets at $\delta_{\text{H}}$ $3.30$ and $3.31$ ppm assignable to two distinct $\text{CH}_3$ protons of DMSO and six singlets at $\delta_{\text{H}}$ $1.94$, $2.14$, $2.18$, $2.30$, $2.31$, $2.54$ ppm assignable to two distinct $\text{CH}_3$ protons of the xylyl moiety of the guanidine. Two $^{1}\text{H}$ NMR signals for $\text{CH}_3$ protons of DMSO in XVII can be interpreted
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by invoking both the steric overcrowding and unsymmetric methyl substitution pattern of the xylyl ring in the guanidine. The \(^{13}\)C NMR pattern of XIV, XVI–XVIII are identical and hence the \(^{13}\)C NMR spectrum of XIV is shown as a representative example in Figure 2.3.9. All these compounds revealed a singlet around \(\delta_c 154\) ppm presumably assignable to the carbon nucleus of the CN\(_3\) core of the guanidine.

**Scheme 2.3.3** Solution Conformers of XV

\[
\begin{align*}
\text{cis, anti-anti} & \quad \text{cis, syn-anti}
\end{align*}
\]

**Scheme 2.3.4** Solution conformers of XVI

\[
\begin{align*}
\text{trans, anti-anti} & \quad \text{cis, anti-anti}
\end{align*}
\]
Chapter 2: Results and Discussion

Figure 2.3.6 $^1$H NMR spectrum of XIV (300 MHz, CDCl$_3$). The symbol * indicates the signal of adventitious $H_2$O protons.
Figure 2.3.6 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XIV in 1.4–4.2 ppm region. The symbol $^*$ indicates the signal of adventitious H$_2$O protons.
Figure 2.3.6 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XIV in 5.6–8.0 ppm region.
Figure 2.3.7 $^1$H NMR spectrum of XV (300 MHz, CDCl$_3$). The symbol * indicates the signal of adventitious $H_2$O protons.
Figure 2.3.7 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XV in 2.8–4.2 ppm region.
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Figure: 2.3.7 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XV in 6.0–8.5 ppm region.
Figure 2.3.8 The $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XVII. The symbol * indicates the signal of adventitious $H_2$O protons.
Figure 2.3.8 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XVII in 1.0–3.5 ppm region. The symbol * indicates the signal of adventitious $H_2$O protons.
Figure 2.3.8 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XVII in 5.0–8.0 ppm region.
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Figure 2.3.9 $^{13}$C NMR spectrum of XIV (100.5 MHz, CDCl$_3$).
Figure 2.3.9 Expansion of the $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XIV in 124–136 ppm region.
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Figure 2.3.9 Expansion of the $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XIV in 17–44 ppm region.
2.3.3.2 Cycloplatination versus Substitution Reactions

The reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with one equiv of LH₂²-anisyl in the presence of one equiv of NaOAc carried out in methanol under reflux condition for 3 h afforded six-membered [C,N] platinacycle, [Pt{κ²(C,N)-C₆H₃(OMe)-3(NHC(NHAr)(=NAr))-2}Cl(S(O)Me₂)] (XX) in 93% yield and the same reaction carried out with LH₂²-tolyl afforded acetate substitution product, trans-[(AcO)Pt(S(O)Me)(LH₂²-tolyl)] (XXIII) in 93% yield. Interestingly, the reaction of XIV with one equivalent of NaOAc in methanol under reflux condition for 3 h afforded XXIII in 92% yield. The authenticity of XXIII prepared by this route was verified by ¹H and ¹³C NMR data. The reaction of reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with one equiv of LH₂²-anisyl in the absence of NaOAc carried out in methanol under reflux condition for 12 h afforded platinacycle, XX. Therefore, it appears that the role of NaOAc is to accelerate the cycloplatination reaction. LH₂²-anisyl is sterically less hindered than LH₂²-tolyl and these guandines possess distinct conformational feature (see above). Further, LH₂²-tolyl and LH₂²,5-xylyl were shown to possess anti-anti αβα conformation and bulkier than LH₂⁴-tolyl and the latter was shown to possess anti-anti conformation in the solid state. It would be of interest to carry out the aforementioned metalation reaction with LH₂²,5-xylyl and LH₂⁴-tolyl to investigate whether their conformational resemblance with LH₂²-tolyl has any influence upon the nature of the product, i.e. substitution product or cyclometalation product. The reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with one equiv of LH₂⁴-tolyl in the presence of one equiv of NaOAc carried out in methanol under reflux condition for 3 h afforded cis-[(AcO)ClPt(S(O)Me)(LH₂⁴-tolyl)] (XXIV) as light greenish yellow crystals in 93% yield. An analogous reaction carried out with LH₂²,5-xylyl afforded a gummy material and no new product could be isolated from the reaction mixture.

The separate reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with one equiv of LH₂²-tolyl or LH₂²,5-xylyl carried out separately in the presence of one equiv of NaOAc in methanol under reflux condition for 12 h afforded six-membered [C,N] platinacycles [Pt{κ²(C,N)-C₆H₃Me-3(NHC(NHAr)(=NAr))-2}Cl(S(O)Me₂)] (Ar = 2-MeC₆H₄; XXI) and [Pt{κ²(C,N)-C₆H₂Me₂-3,6(NHC(NHAr)(=NAr))-2}Cl(S(O)Me₂)] (Ar = 2,5-Me₂C₆H₃; XXII) in 89 and 93% yield, respectively. The reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with one
equiv of $\text{LH}_2^{4\text{-tolyl}}$ in the presence of one equiv of NaOAc carried out in methanol under reflux condition for 12 h afforded gummy material from which no new products could be isolated. The aforementioned cycloplatination and OAc$^-$ substitution reactions are illustrated in Scheme 2.3.5. The yield of the platinacycles are remarkable because cycloplatination reaction takes usually longer reaction period and sometimes even up to four weeks and requires relatively forcing conditions. The reaction of $\text{cis-}[\text{Cl}_2\text{Pt}((\text{S(O)Me}_2)_2]$ with one equiv of $\text{LH}_2^{2,6\text{-xylyl}}$ in the presence of one equiv of NaOAc in methanol under reflux condition even after 36 h afforded neither cycloplatinated product nor substitution product but led to the formation of the adduct XVIII and unreacted $\text{LH}_2^{2,6\text{-xylyl}}$ as revealed by $^1\text{H}$ NMR data.

2.3.3.2.1 Single Crystal X-ray Diffraction Data

Platinacycle XX was crystallized from methanol/CH$_2$Cl$_2$ mixture at ambient temperature over a period of several days to afford pale yellow crystals. The molecular structure of XX is depicted in Figure 2.3.10. Selected bond distances and bond angles are listed in Table 2.3.9. The platinum atom is surrounded by the imine nitrogen, aryl carbon, chloride and the sulfur atom of S(O)Me$_2$ and revealed a distorted square planar geometry. The S(O)Me$_2$ is coordinated to the platinum atom in cis relation with respect to the Pt–C bond due to antisymbiosis or transphobia.$^{42,43}$ According antisymbiosis, two soft ligands in mutual trans position will have a destabilizing effect on each other when attached to class b metal atoms.$^{42}$ A closer look at the stereochemistry of the platinum atom in the related six-membered [$C,N$] platinacycles$^{2a,44,46}$ and in the related six-membered [$C,N$] palladacycles$^{30}$ suggests that both steric bulk and global hardness of the surrounding ligands influence the stereochemistry of the platinum atom in XX.

The six-membered "$[C,N]$Pt$^\alpha$" ring in XX revealed a pseudo boat $\alpha$ conformation with N1, C1, C9 and C14 atoms defining the basal plane of the boat while Pt1 and N2 atoms defining the tips of the boat as shown in the inset of Figure 2.3.10. The Pt–N distance, 2.061(3) Å is comparable with the predicted value of 2.06 Å.$^{32}$ The Pt–C distance, 2.015(4) Å in XX is slightly shorter than the predicted value of 2.06 Å (covalent radius of
Scheme 2.3.5 Cycloplatination versus Substitution Reactions

Ar = 2-(MeO)C₆H₄
2-MeC₆H₄
2,5-Me₂C₆H₃

Ar = 2-(MeO)C₆H₄
2-MeC₆H₄
2,5-Me₂C₆H₃
Figure 2.3.10 An ORTEP representation of XX at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity. Inset: The pseudo boat conformation of the six-membered "[C,N]Pt" ring.
Table 2.3.9 Selected Bond Distances (Å) and Bond Angles (deg.) for Platinacycle XX.

<table>
<thead>
<tr>
<th></th>
<th>XX</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1-C1</td>
<td>2.404(8)</td>
<td>N1-Pt1-Cl1</td>
<td>89.93(7)</td>
</tr>
<tr>
<td>Pt1-N1</td>
<td>2.061(3)</td>
<td>N1-Pt1-S1</td>
<td>175.11(8)</td>
</tr>
<tr>
<td>Pt1-S1</td>
<td>2.217(9)</td>
<td>S1-Pt1-Cl1</td>
<td>87.93(3)</td>
</tr>
<tr>
<td>Pt1-C14</td>
<td>2.016(3)</td>
<td>N1-Pt1-C14</td>
<td>87.29(1)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.312(4)</td>
<td>S1-Pt1-C14</td>
<td>94.75(1)</td>
</tr>
<tr>
<td>N2-C1</td>
<td>1.353(4)</td>
<td>C11-Pt1-C14</td>
<td>177.04(1)</td>
</tr>
<tr>
<td>N3-C1</td>
<td>1.362(4)</td>
<td>C1-N1-C2</td>
<td>119.6(3)</td>
</tr>
<tr>
<td>N1-C2</td>
<td>1.442(4)</td>
<td>C1-N2-C9</td>
<td>123.80(3)</td>
</tr>
<tr>
<td>N2-C9</td>
<td>1.414(4)</td>
<td>C1-N3-C16</td>
<td>128.10(3)</td>
</tr>
<tr>
<td>N3-C16</td>
<td>1.418(5)</td>
<td>C1-N1-Pt1</td>
<td>118.00(2)</td>
</tr>
<tr>
<td>S1-O4</td>
<td>1.465(3)</td>
<td>C2-N1-Pt1</td>
<td>122.30(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C9-C14-Pt1</td>
<td>118.70(2)</td>
</tr>
</tbody>
</table>

\(r(\text{Pt(II)}): 1.36\,\text{Å}; \) covalent radius of \(r(\text{C}(sp^2)) \approx 0.70\,\text{Å}\)^32 indicating some degree of Pt–C multiple character. The \(\Delta_{CN}: 0.041(6)\,\text{Å}\) value in XX is slightly smaller than \(\Delta_{CN}': 0.050(6)\,\text{Å}\) value and these values are smaller than the corresponding values known for guanidine derived six-membered [C,N] palladacycle, \([\text{Pd}\{\kappa^2(\text{C,N})-\text{C}_6\text{H}_3(\text{OMe})-3(\text{NHC(NHAr)(=NAr)})-2]\text{Cl(NC}_3\text{H}_3\text{Me}_2-2,6)] (\text{Ar} = 2-(\text{MeO})\text{C}_6\text{H}_4 (35); \Delta_{CN}: 0.064(6)\,\text{Å}; \Delta_{CN}': 0.065(6)\,\text{Å}) but greater than those known for \([\text{Pd}\{\kappa^2(\text{C,N})-\text{C}_6\text{H}_3(\text{OMe})-3(\text{NHC(NHAr)(=NAr)})-2]\text{Cl(NC}_3\text{H}_3\text{Me}_2-2,4)] (\text{Ar} = 2-(\text{MeO})\text{C}_6\text{H}_4 (36); \Delta_{CN}: 0.026(1)\,\text{Å}; \Delta_{CN}': 0.038(1)\,\text{Å}).^{30}\) It is to be noted that the palladium atom in 35 and 36 was shown to possess a trans geometry and this was explained by invoking global hardness of the substituents surrounding the palladium atom. The amino nitrogens in XX are planar. The sulfur atom of DMSO is shown to possess a tetrahedral geometry. The bond parameters around the platinum atom in XX are comparable with those observed in the related cis-[ClPt(C,N)(S(O)Me2)].\(^{45}\) Platinacycle XX is shown to possess numerous noncovalent interactions as illustrated in Figures S2.3.15 and S2.3.16.

The substitution product XXIII was obtained as light greenish yellow crystals from methanol/chloroform mixture at ambient temperature over a period of several hours. The molecular structure of XXIII is depicted in Figure 2.3.11. Selected bond distances and bond angles are listed in Table 2.3.10. The platinum atom in XXIII is surrounded by the
Figure 2.3.11 An ORTEP representation of XXIII at the 50% probability level. Only the hydrogen atoms of the amino moieties are shown for clarity.
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Table 2.3.10 Selected Bond Distances (Å) and Bond Angles (deg.) for Substitution Product XXIII

<table>
<thead>
<tr>
<th></th>
<th>XXIII</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1-C1</td>
<td>2.305(2)</td>
<td>Cl1-Pt1-O2</td>
</tr>
<tr>
<td>Pt1-O2</td>
<td>2.047(4)</td>
<td>S1-Pt1-C11</td>
</tr>
<tr>
<td>Pt1-S1</td>
<td>2.188(5)</td>
<td>S1-Pt1-O2</td>
</tr>
<tr>
<td>Pt1-N1</td>
<td>2.026(5)</td>
<td>N1-Pt1-C11</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.307(7)</td>
<td>N1-Pt1-O2</td>
</tr>
<tr>
<td>N2-C1</td>
<td>1.361(7)</td>
<td>N1-Pt1-S1</td>
</tr>
<tr>
<td>N3-C1</td>
<td>1.363(7)</td>
<td>C1-N1-Pt1</td>
</tr>
<tr>
<td>N1-C2</td>
<td>1.437(7)</td>
<td>C1-N1-C2</td>
</tr>
<tr>
<td>N2-C9</td>
<td>1.421(7)</td>
<td>C1-N2-C9</td>
</tr>
<tr>
<td>N3-C16</td>
<td>1.419(7)</td>
<td>C1-N3-C16</td>
</tr>
<tr>
<td>S1-O1</td>
<td>1.466(4)</td>
<td>C2-N1-Pt1</td>
</tr>
<tr>
<td>O2-C25</td>
<td>1.295(7)</td>
<td>Pt1-O2-C25</td>
</tr>
<tr>
<td>O3-C25</td>
<td>1.237(7)</td>
<td>O2-C25-O3</td>
</tr>
<tr>
<td>C25-C26</td>
<td>1.509(8)</td>
<td>O2-C25-C26</td>
</tr>
</tbody>
</table>

imine nitrogen of the guanidine, oxygen atom of the monodentate acetate, chloride and the sulfur atom of DMSO. The bond parameters around the platinum atom indicate a slightly distorted square planar geometry.

The oxygen atom of the acetate and the sulfur atom of DMSO are placed trans to each other around the platinum atom as are the imine nitrogen of the guanidine and the chloride. Remarkably, the platinum atom revealed a cis geometry that contrasts with the trans geometry of the platinum atom observed in XIV (see later). Guanidine was shown to exhibit anti-anti conformation as observed in XIV. The Pt–O distance, 2.047(4) Å in XXIII is slightly longer than the predicted value of 1.99 Å (covalent radius of r(Pt(II)): 1.36 Å; covalent radius of r(O(sp³)) : 0.63 Å)³² and that found in trans-[Pt(OAc)₂(isopropylamine)(N-methylimidazole)](2.007(3); 2.008(3)Å)⁴⁷ due to the trans influence of sulfur bound DMSO, but shorter than that observed in [Pt{FeCp(σ,η⁵-C₅H₅CH₂NMe₂)}(DMSO)(OAc)] (2.115(5)Å)⁴⁸ due to the greater trans influence of the aryl carbon in this complex. The ΔCN: 0.054(10) Å value is comparable with ΔCN’: 0.056(10) Å value. Both amino nitrogens are planar. The ρ: 0.96 value in conjunction with the values of ΔCN and ΔCN’ and planarity of the amino nitrogen in XXIII suggest a partial n–π conjugation between the lone pair of NHAr moieties with C=N π* orbital.
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The substitution product XXIII is shown to possess numerous noncovalent interactions as illustrated in Figures S2.3.17 and S2.3.18.

2.3.3.2.2 IR Studies

The IR spectral data of platinacycles XX–XXII are listed in Table 2.3.11. The guanidine moiety in platinacycles XX–XXII revealed two bands in the interval 3436–3293 cm\(^{-1}\) assignable to two distinct NH moieties and one band in the interval 1620–1604 cm\(^{-1}\) assignable to the C=N moiety. The IR spectrum of XX–XXII also revealed one band in the interval 1117–1142 cm\(^{-1}\) anticipated for sulfur coordinated DMSO.\(^{33}\)

<table>
<thead>
<tr>
<th>Platinacyle</th>
<th>(\nu)(NH)</th>
<th>(\nu)(C=N)</th>
<th>(\nu)(S=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>3436, 3392</td>
<td>1618</td>
<td>1117</td>
</tr>
<tr>
<td>XXI</td>
<td>3433, 3378</td>
<td>1620</td>
<td>1142</td>
</tr>
<tr>
<td>XXII</td>
<td>3385, 3293</td>
<td>1604</td>
<td>1138</td>
</tr>
</tbody>
</table>

The IR spectrum of XXIII revealed two bands at 3440, 3384 cm\(^{-1}\) while that of XXIV revealed one band at 3381 cm\(^{-1}\) assignable to two distinct NH moieties. A pair of bands was observed at 1623, and 1384 cm\(^{-1}\) (XXIII) and 1626, and 1377 cm\(^{-1}\) (XXIV) for the acetate moiety assignable to \(\nu_a\)(OCO), and \(\nu_s\)(OCO) stretch, respectively. The \(\Delta \nu = \nu_a(\text{OCO}) - \nu_s(\text{OCO}) = 239 \text{ cm}^{-1}\) (XXIII), and 249 cm\(^{-1}\) (XXIV) values indicate monodentate acetate coordination mode in both complexes.\(^{49}\) The IR spectrum of XXIII and XXIV also revealed a band at 1603 and 1604 cm\(^{-1}\), respectively assignable to the C=N moiety and one band at 1132 and 1134 cm\(^{-1}\), respectively assignable to the S=O stretch of DMSO. The \(\nu(S=O)\) value of XXIII and XXIV indicates sulfur coordination to the platinum.\(^{33}\)

2.3.3.2.3 ESI-MS Studies

Platinacycles XX–XXII were subjected to ESI-MS study to obtain the information regarding the integrity and dissociative nature of these compounds in solution. The most informative peaks are listed in Table 2.3.12. As a representative example, the ESI-MS spectrum of XVIII is illustrated in Figure 2.3.12. Platinacycle XX revealed a peak at m/z (intensity %): 608.6355 (53) assignable to [M + H – S(O)Me\(_2\)]\(^+\) and that of XXI revealed two peaks at m/z (intensity %): 642.1862 (20) and 636.1373 (45) assignable to [M + Li
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- 2H]^+ and [M]^+, respectively. Platinacycle XXII revealed two peaks at m/z (intensity %): 721.2141 (72) and 680.1875 (93) assignable to [M + 3H + K]^+ and [M + H]^+, respectively. ESI-MS spectrum of XXIII revealed a peak at m/z (intensity %): 698.4891 (25) assignable to [M + H]^+ while that of XXIV revealed peaks at m/z (intensity %): 1311.3 (10) and 638.2 (26) assignable to [Pt₂(μ₂-κ²N:\κ¹N'-LH₄-tolyl)₂(μ₂-κ¹O:\κ¹O'-OAc)(DMSO)₂ + Li + K + 3H]^+ and [M − OAc]^+, respectively (see Scheme 2.3.6).

Table 2.3.12 Selected m/z values of Platinacycles XX–XXII obtained from ESI-MS Data. Intensity (%) is given in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>m/z values</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>608.6355(53), [M + H – S(O)Me₂]^+; 571.7191 (100), [M – Cl – S(O)Me₂]^+; 554.7188 (72), [M – HCl – Me]^+</td>
</tr>
<tr>
<td>XXI</td>
<td>642.1862 (20), [M + Li – 2H]^+; 638.1377 (22), [M + H]^+; 636.1373 (45) [M]^+; 619.1720 (15), [M – 3H, Me]^+; 601.1634 (100), [M – Cl]^+</td>
</tr>
<tr>
<td>XXII</td>
<td>721.2141 (72), [M + 3H + K]^+; 680.1875 (93), [M + H]^+; 643.2024 (43), [M – Cl]^+</td>
</tr>
<tr>
<td>XXIII</td>
<td>735.3175 (8), [M + H + K]^+; 698.4891 (25) [M + H]^+; 661.6127 (20), [M – Cl]</td>
</tr>
<tr>
<td>XXIV</td>
<td>1311.3 (10), [Pt₂(μ₂-κ²N:\κ¹N'-LH₄-tolyl)₂(μ₂-κ¹O:\κ¹O'-OAc)(DMSO)₂ + Li + K + 3H]^+, 638.2 (26), [M − OAc]^+; 602.2 (53), [M − Cl − OAc]^+; 564.2 (15), [M + K − Cl – S(O)Me₂ – OAc]^+</td>
</tr>
</tbody>
</table>

Scheme 2.3.6
Figure 2.3.12 The ESI MS Mass Spectrum of XX.
Figure 2.3.12 Expansion of the ESI MS Mass Spectrum of XX.
2.3.3.2.4 NMR Studies

The $^{195}$Pt{${}^1$H} NMR spectrum of XX revealed one peak at $\delta_{Pt} = -3737$ ppm as shown in Figure S2.3.19 and this value is upfield shifted relative to that observed for the adduct XV (cis,anti-anti isomer; $\delta_{Pt} = -2721$ ppm). This trend is in line with the literature trend reported for the adduct of the type [Cl$_2$PtL(S(O)Me$_2$)$_2$] and platinacycle of the type [ClPt(C,N)(S(O)Me$_2$)$_2$] pair.$^{4b,5a,8c,40b,50}$ The $\delta_{Pt}$ value observed for XX is comparable with that reported for the related six-membered indole-fused amine derived [C,N] platinacycles.$^{51}$ The $^1$H and $^{13}$C NMR spectra of XX are illustrated in Figures 2.3.13 and 2.3.14, respectively. As can be seen, platinacycle XX is shown to exist as a single isomer in solution. The $^1$H NMR spectrum of XX revealed two broad peaks at $\delta_{H} 3.36$ and 3.48 ppm assignable to two magnetically nonequivalent CH$_3$ protons of DMSO and this spectral feature suggest that the solid state structure is probably retained in solution. Additionally, three singlets were observed at $\delta_{H} 3.79$, 3.86, and 4.08 ppm assignable to OCH$_3$ protons of the guanidine moiety. The $^{13}$C NMR spectrum of XX revealed two singlets at $\delta_{C} 46.2$ and 46.8 ppm assignable to two magnetically nonequivalent CH$_3$ carbon of DMSO. Further, three singlets were observed at $\delta_{C} 55.2$, 55.8, and 56.1 ppm assignable to three magnetically nonequivalent OCH$_3$ carbon of the guanidine moiety.

It is to be noted that the guanidine derived six-membered [C,N] palladacycles, 35 and 36 revealed the presence of two boat conformers that interconvert via a planar intermediate as revealed by a detailed $^1$H NMR studies and this spectral feature contrasts with that observed in XX (i.e. observance of a single isomer) as revealed by $^1$H and $^{13}$C NMR data. This could be attributed to the presence of bulkier and more strongly $\pi$-accepting DMSO in XX.

The $^1$H NMR spectrum of XXI indicated the presence of four major isomers in about 1:1:1:1 ratios in solution as estimated from integrals of CH$_3$ protons of tolyl substituent. Totally twelve singlets were observed at $\delta_{H} 1.642$, 1.932, 1.960, 2.037, 2.040, 2.112, 2.240, 2.273, 2.330, 2.487, 2.588, and 2.612 ppm assignable to CH$_3$ protons of the tolyl substituent. The $^1$H NMR spectrum of XXI also revealed twelve singlets at $\delta_{H} 1.885$, 1.899, 1.976, 2.059, 2.097, 2.137, 2.200, 2.220, 2.429, 2.570, 2.654, 2.696 ppm and their assignment to a particular conformer is not straightforward. Hence, platinacycle XXI was subjected to the $^{195}$Pt NMR study. The $^{195}$Pt{${}^1$H} NMR spectrum of XXI revealed seven
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signals at $\delta_{\text{H}}$ - 2645 (minor), - 2710 (major), - 2760 (minor), - 2839 (minor), - 2851 (minor), - 2958 (major), and - 2995 (minor) as illustrated in Figure S2.3.20. Platinacycle XXI upon further crystallization in methanol/chloroform over a period of seven days afforded a light yellow crystalline solid. The $^1$H NMR spectrum of this material is illustrated in Figure 2.3.15. The $^1$H NMR spectrum of the solid revealed three singlets at $\delta_{\text{H}}$ 1.964, 2.334, 2.595 ppm assignable to CH$_3$ protons of tolyl substituent, two singlets at $\delta_{\text{H}}$ 3.302, 3.315 ppm assignable to CH$_3$ protons of DMSO and two singlets $\delta_{\text{H}}$ 5.614, 7.786 ppm assignable to NH protons in addition to signals in the $\delta_{\text{H}}$ 6.831–7.760 ppm range assignable to the aryl protons. This pattern clearly indicated the presence of a single conformer in solution. The $^1$H NMR of platinacycle XXII indicated the presence of four isomers (major, intermediate and minor) in about 1.0:0.38:0.16:0.08 ratios in solution as estimated from the $^1$H NMR integrals of CH$_3$ protons of DMSO. The details pertinent to the assignment of $\delta_{\text{H}}$ to all four isomers are given in Experimental Section.

The $^{195}$Pt{$^1$H} NMR spectrum of XXII revealed three signals at $\delta_{\text{Pt}}$ -2647 (minor 1), -2713 (intermediate), and -2951 (major) as illustrated in Figure S2.3.21. The $\delta_{\text{Pt}}$ values of XXI and XXII are more deshielded than that observed for XX. This data indicates that DMSO in XXI and XXII is coordinated to the platinum atom probably via the oxygen atom rather than through sulfur atom in order to minimize the steric repulsion with the o-Me substituent of the =NAr moiety. It has been suggested that steric factor induces O-bounding in metal sulfoxide complexes.$^{33b}$ The DMSO in XXI and XXII is perhaps bound to the platinum atom via sulfur in the solid state as evidenced by IR data but upon dissolving these platinacycles in CDCl$_3$ appear to isomerise to the O-bonded isomers. The $\delta_{\text{Pt}}$ -1459 ppm value reported for S bound mer-[Cl$_3$Pt(C,N)(S(O)Me$_2$)] differs significantly from that of O-bound mer-[Cl$_3$Pt(C,N)(O=SMe$_2$)] ($\delta_{\text{Pt}}$ -774 ppm) but not so significantly from S bound fac-[Cl$_3$Pt(C,N)(S(O)Me$_2$)] ($\delta_{\text{Pt}}$ -1609 ppm).$^{32}$ Five-membered [C,N] palladacycles with O-bonded DMSO configuration is known in the literature.$^{12,51}$ In principle, four conformers namely, $\alpha_1$, $\beta_1$, $\alpha_2$, $\beta_2$ are possible for XX as shown in Chart 2.3.2. In these four conformers, DMSO is S-bonded to platinum and is
Figure 2.3.13 $^1$H NMR spectrum of XX (300 MHz, CDCl$_3$). The symbol * indicates the signal of adventitious $H_2O$ protons.
Figure 2.3.13 Expansion of the $^1$H NMR spectrum (300 MHz, CDCl$_3$) of XX in 3.0–8.5 ppm region.
Figure 2.3.14 $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XX.
Figure 2.3.14 Expansion of the $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XX in 106–136 ppm region.
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Figure 2.3.14 Expansion of the $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XX in 44–57 ppm region.
Figure 2.3.15 $^1$H NMR spectrum (400 MHz, CDCl$_3$) of one of the crystals of XXI.
Figure 2.3.15 Expansion of the $^1$H NMR spectrum (400 MHz, CDCl$_3$) of one of the crystals of XXI in 1.9–3.4 ppm region.
Figure 2.3.15 Expansion of the $^1$H NMR spectrum (400 MHz, CDCl$_3$) of one of the crystals of XXI in 6.7–7.9 ppm region.
placed \textit{trans} to the imine nitrogen. Platinacycle XX crystallized as \(\alpha1\) conformer in the solid state (see Figure 2.3.10). However, twelve conformers are possible for XXI and XXII, four already discussed in Chart 2.3.2. The structures of remaining eight conformers are illustrated in Chart 2.3.3. In \(\alpha3\), \(\beta3\), \(\alpha4\), \(\beta4\), conformers DMSO is O-bonded to the platinum atom and is placed \textit{trans} to the imine nitrogen. In \(\alpha5\), \(\beta5\), \(\alpha6\), \(\beta6\) conformers DMSO is O-bonded to the platinum and is placed \textit{cis} to the imine nitrogen. The difference in solution behavior of XX and those of XXI and XXII can be explained as follows. The imine nitrogen atom of the guanidine in XX is probably harder than the imine nitrogen atom of the guanidine in XXI and XXII. The \(\alpha1\) conformer appears to be decided by antisymbiosis. The multiple solution conformers of XXI and XXII appear to arise from the contribution of steric factor, antisymbiosis, and solvation effects (see below).

The \(^{195}\text{Pt}\{^1\text{H}\}\) NMR spectra of XXIII and XXIV are illustrated in Figures S2.3.22 and S2.3.23, respectively. The \(^{195}\text{Pt}\{^1\text{H}\}\) NMR spectrum of XXIII revealed a peak at \(\delta_{\text{Pt}} = 2718\) ppm and this value is more deshielded than that observed for the adduct XIV (\(\delta_{\text{Pt}} = 2967\) ppm). The \(^{195}\text{Pt}\{^1\text{H}\}\) NMR spectrum of XXIV revealed a peak at \(\delta_{\text{Pt}} = 2891\) ppm and this value is more deshielded than that observed for \textit{trans} isomer of XVI but comparable to that observed for the \textit{cis} isomer of XVI (\(\delta_{\text{Pt}} = 3009\) (\textit{trans}), \(\delta_{\text{Pt}} = 2898\) (\textit{cis}) ppm). The \(\Delta\delta_{\text{Pt}} = \delta_{\text{Pt}} (\text{cis-XVI}) - \delta_{\text{Pt}} (\text{XXIV}) = -2898 -(-2891) = -7\) ppm compares fairly well with the \(\Delta\delta_{\text{N}}\) observed between \textit{cis}-\([\text{Cl}_2\text{Pt}(N,N')]\) and \textit{cis}-\([(\text{AcO})\text{ClPt}(N,N')\)] \((N,N':\text{Ferrocene derived amino imine}; \Delta\delta_{\text{Pt}}: +7\) ppm) pair.\(^{5h}\)

Proton NMR spectrum of XXIII revealed four singlets at \(\delta_{\text{H}} 1.96, 2.13, 2.30,\) and 2.52 ppm in about 1:1:1:1 ratios and that of XXIV revealed four singlets at \(\delta_{\text{H}} 2.10, 2.14, 2.20,\) and 2.30 ppm in about 1:1:1:1 ratios both assignable to \(\text{CH}_3\) protons of the guanidine and \(\text{OAc}\) moieties. Two separate singlets were observed at \(\delta_{\text{H}} 3.34,\) and 3.53 ppm (XXIII) and at \(\delta_{\text{H}} 3.27,\) and 3.34 ppm (XXIV) assignable to \(\text{CH}_3\) protons of DMSO and two separate singlets were observed at \(\delta_{\text{H}} 5.64,\) and 10.60 ppm (XXIII) and at \(\delta_{\text{H}} 5.90,\) and 8.20 ppm (XXIV) assignable to two chemically nonequivalent NH protons of
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The observed spectral features of XXIII indicate that the solid state structure is probably retained in solution as well.

The $^{13}$C NMR spectrum of XXIII is illustrated in Figure 2.3.16. As can be seen, four singlets were observed at $\delta_C$ 17.60, 18.15, 19.35, 20.88 ppm assignable to CH$_3$ carbon of the guanidine and the acetate moieties. Further, one singlet was observed at $\delta_C$ 43.5 ppm assignable to CH$_3$ carbon of DMSO and one singlet was observed at $\delta_C$ 176.8 ppm assignable to OC(O) carbon of the acetate moiety. The $^{13}$C NMR spectrum of XXIV revealed one broad peak at $\delta_C$ 20.9 ppm assignable to CH$_3$ carbon nuclei of the guanidine and one singlet at $\delta_C$ 21.1 ppm assignable to CH$_3$ carbon of the acetate moiety. The CH$_3$ carbon of DMSO and OCO carbon of the acetate moiety revealed a singlet at $\delta_C$ 43.7 and 177.4 ppm, respectively. Compounds XXIII and XXIV also revealed several peaks in 124.58–154.55 and 122.6–153.7 ppm intervals assignable to the aryl and CN$_3$ carbon of the guanidine moiety.

Chart 2.3.2
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Chart 2.3.3

R
XXI
Me
H
XXII
Me
Me
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The reaction of platinacycle XX with one equivalent of triphenylphosphine (Ph₃P) in CDCl₃ and toluene mixture under reflux condition for 12 h afforded six-membered [C,N] platinacycle $\text{[Pt}\{\chi^2(C,N)-C_6H_3(OMe)-3(NHC(NHAr)(=NAr))-2\}\text{Cl}(\text{Ph}_3\text{P})\}$ (XXV); (Ar = 2-(MeO)C₆H₃) in 93% yield as illustrated in Scheme 2.3.7. Platinacycle XXV was characterised by NMR ($^1$H and $^{31}$P) only due to paucity of the sample. The $^1$H NMR spectrum of XXV revealed three isomers in about 1:2.6:6 ratios in solution as identified from the integrals of OCH₃ protons of the guanidine. The $^{31}$P NMR spectrum of platinacycle XXV revealed one peak at $\delta$P 21.1 (J$_{P-Pt}$ 4355 Hz) this J$_{P-Pt}$ value is comparable with that reported related imine derived six membered [C,N] platinacyle.²c

Scheme 2.3.7

2.3.4 Mechanistic Aspects

The mechanism of C-H activation involving platinum complexes has been studied intensively.⁵⁴,⁵⁵ In 1974 Shaw and co-workers first time used NaOAc as a stoichiometric reagent in cyclometalation reaction of cis-[Cl₂Pt(phosphine)$_2$].⁵⁶ Since then NaOAc has became one of the essential reagents in both stoichiometric and catalytic C–H activation process.⁵⁷ The reaction of cis-[Cl₂Pt(S(O)Me)$_2$] with N-donor ligand in solvent such as toluene was shown to afford cis/trans-[Cl₂Pt(S(O)Me)₂L] and the same reaction carried out in toluene/methanol mixture in the presence of NaOAc was shown to afford the cycloplatinated product, [ClPt(S(O)Me₂)(C,N)]. Cycloplatination reaction was successful in the absence of NaOAc when the N-donor ligands possess electron releasing substituents⁵⁸ or electron releasing and sterically encumbered substituent.⁵⁹
Figure 2.3.16 $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XXIII.
Figure 2.3.16 Expansion of the $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XXIII in 124–136 ppm region.
Figure 2.3.16 Expansion of the $^{13}$C NMR spectrum (100.5 MHz, CDCl$_3$) of XXIII in 14–44 ppm region.
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Cycloplatination of aryl oxime ligands with cis-[Cl₂Pt(S(O)Me₂)₂] was shown to be successful even in the absence of NaOAc due to the better orientation of the aryl ring in trans-[ClPt(DMSO)(aryloxime)] towards the platinum(II) atom.¹¹ NaOAc was suggested to play a dual role, as a nucleophile and as an internal base in C–H activation reactions involving platinum(II) precursors and N-donor ligands.⁴a,⁴d

Cycloplatination was shown to be successful for those imine ligands that lead to the formation of trans-[Cl₂Pt(DMSO)(L)] (L = N-donor imine ligand) while the process is inhibited for those ligands that lead to the formation of cis-[Cl₂Pt(DMSO)(L)].²f,¹¹ Formation of either cis or trans [Cl₂Pt(DMSO)₂] was related to steric effect and to the E or Z configuration of the C=N bond.²f The preorganisation and conformational aspects of imine bound to palladium/platinum were often discussed in relation to the feasibility of successful C–H activation process. The E-configuration, rather than Z configuration of the imine ligand in the precursor complex of the type [Cl₂Pt(DMSO)(L)] (L = N-donor imine ligand) or [Cl₂Pt(N,E)] (E: nitrogen and sulfur donor atoms) was shown to be a better preorganised for C–H activation process. Trans-[Cl₂Pt(DMSO)(L)] (L = N-donor imine ligand) with the imine in Z configuration was shown to rearrange to the trans adduct with imine in E configuration before cyclometalation process.⁴d,³g,⁵h,⁷a,⁷c

Alternatively, a free rotation around the Cipso–Camine bond of [Cl₂Pt(DMSO)(L)] (L = Ferrocene derived N-donor imine ligand)⁴c,⁸c or a free rotation around the Cipso–Camine of [Cl₂Pt(DMSO)(L)] (L = Ferrocene derived N-donor amine ligand)⁶¹ was suggested to explain the formation of a pair of ferrocene derived diastereomeric [C,N] platinacycles. The coordinated acetate of [XX'Pt(N,N')] (N,N': bidenate amino imine ligand; X = Cl; X' = OAc; X = X' = OAc) was shown to assist the preorganisation of the amino imine ligand from Z to E configuration and the dangling oxygen of the coordinated OAc was shown to favor an intramolecular C–H activation reaction via a tetracentred transition state involving the acetato ligand, the metal centre, the cyclometallating carbon and the hydrogen.³d C. Lopez et al have isolated acetate substitution product albeit in very low yield from a reaction involving cis-[Cl₂Pt(S(O)Me₂)₂] and ferrocene derived amino imine ligand in the presence of NaOAc.⁵h Compound XXIII represents the first structurally characterized substitution product in the cyclometalation reaction mediated by NaOAc.
One question that occurred to our mind is why the geometry of the platinum(II) atom in XIV, XVII, and XVIII and perhaps in XVI is trans and switches to cis in XV and XXIII. Factors governing the geometry of the platinum atom in [X₂Pt(PR₃)₂] have been discussed with the aid of DFT calculations and it has been shown that the cis-trans preferences were ascribed to the combination of electrostatics, π-back bonding, antisymbiosis, and solvation effects. The global hardness introduced by R. G. Pearson can be invoked to explain the difference in geometry of the platinum atom in XIV, XVII, XVIII and XV and XXIII as has been invoked to explain the trans and cis chelation of NHC-derived bis(amidiniophosphine) ligand in rhodium(I) complexes. In XIV, XVII, and XVIII, the soft sulfur atom of DMSO prefers the harder imine nitrogen of the guanidine trans it and that in XV prefers harder chloride due to antisymbiosis. The steric factor does appear to play a key role in deciding the geometry of the platinum atom as (i) trans geometry is observed for the platinum atom in XVI as suggested by ¹⁹⁵Pt NMR data and (ii) cis geometry is observed for the platinum atom in XXIII as determined by X-ray diffraction data. Why there is a geometry switch of the platinum(II) atom on going from XIV to XXIII? Perhaps solvation effect can be invoked to explain this feature. Complex XIV was prepared in toluene (ε = 2.38) whereas complex XXIII was prepared in methanol (ε = 33).

The overall mechanism of cyclometalation of sym N,N',N″-triarylguanidine with cis-[Cl₂Pt(S(O)Me₂)₂] is illustrated in Scheme 2.3.8. The reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with sterically more hindered and less basic LH₂²-tolyl, LH₂²,5-xylyl and LH₂²,6-xylyl afforded trans adducts XIV, XVII and XVIII as kinetically controlled products. In the absence of steric protection, more basic LH₂⁴-tolyl upon reaction with cis-[Cl₂Pt(S(O)Me₂)₂] afforded XVI, which was shown be a mixture of trans isomer and small quantity of cis isomer as determined by ¹⁹⁵Pt NMR data. The less basic and sterically less hindered LH₂²-anisyl upon reaction with cis-[Cl₂Pt(S(O)Me₂)₂] give thermodynamic product, XV. This conclusion turns out to be opposite to what has been arrived at by others from the reaction of cis-[Cl₂Pt(S(O)Me₂)₂] with pyridine type Lewis bases. Either cis or trans [Cl₂Pt(S(O)Me₂)(L)] upon reaction with NaOAc in methanol afforded cis-[Cl(AcO)Pt(S(O)Me₂)(L)]. The acetate substitution products of the type XXIII and XXIV, in principle can undergo either C=NAr double bond rotation as noted.
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for the related complexes or C=C=N single bond rotation. We believe that cis-[Cl(AcO)Pt(S(O)Me$_2$)(L)] (L = N,N',N'-triarylguanidine) would not undergo C=C=NR bond rotation as such process does not bring the aryl moiety of one of the NHAr units closer to the coordinated acetate for C=H activation. In an hypothetical cis,syn-anti form of [Cl(AcO)Pt(S(O)Me$_2$)(L)], one of the NHAr units would be pointing towards to C=N unit and hence the aryl ring would be closer to the platinum atom whereas in another hypothetical cis,anti-anti form both NHAr units of the guanidine would be pointing away from the C=N bond and hence from the platinum(II) atom. Therefore, cis, syn-anti form of [Cl(AcO)Pt(S(O)Me$_2$)L] appears to be more preorganised than cis,anti-anti form for successful cyclometalation event. Hence, the acetate substitution product cis-[Cl(AcO)Pt(S(O)Me$_2$)(L)] appears to undergo C=N rotation before forming the platinacycles.

The amine derived six-membered [C,N] platinacycle was suggested to form from trans-[Cl$_2$(NH$_3$)Pt(L)] via $\eta^2$-bonded arene intermediate and $\eta^1$-arenium transition state and such intermediate was presumed to be stabilized due to optimal d-$\pi^*$ orbital overlap. Cylopalladation of dimethylbenzylamine was suggested to involve a Wheland type intermediate that upon intramolecular deprotonation by coordinated acetate to give a 6-membered transition state as suggested by Ryabov and co-workers. Davies and coworkers performed DFT calculations on [Pd(DMBAH)(OAc)$_2$] (DMBA-H = dimethylbenzylamine) and suggested that the interaction between electrophilic Pd(II) centre and the C=H bond was more consistent with an agostic structure, rather than a Wheland or $\eta^1$-arenium intermediate formed by electrophilic attack on the arene ring.

Presumably, platinacycle XX, XXI and XXII were formed from the respective acetate substitution products via elimination of AcOH through AMLA, an acronym used for Ambiphilic Metal Ligand Activation by Davies coworkers. The fact that cis-[Cl$_2$Pt(S(O)Me$_2$)$_2$] fails to cyclometalate $\text{LH}_2^{2,6-\text{xyl}}$ suggests that the adduct XVIII is sterically more encumbered and unable to undergo trans $\rightarrow$ cis isomerisation process. The timescale of platination of $\text{LH}_2^{2-\text{anisyl}}$ is shorter than those involving $\text{LH}_2^{2-\text{tolyl}}$ and $\text{LH}_2^{2,5-\text{xyl}}$ probably due to lesser steric hindrance of the o-anisyl moiety in the former guanidine that permits faster C=N bond rotation of the acetate substitution product such
Scheme 2.3.8 Mechanism of Cycloplatination Reactions
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as XXIII. Fortuitously, the greater steric hindrance of LH$_2$$_2$-toly permitted us to obtain the single crystal X-ray diffraction data for XXIII to better understand the mechanism of C–H activation process. The role of NaOAc is not known clearly although Wu, Crespo, and Lopez indicated that OAc reacts with 1:1 platinum nitrogen donor adduct before C-H activation process.$^{3d,4a,4d,5h}$ The molecular structure of XXIII thus represents the first structurally characterized acetate substitution product of the C–H activation reaction involving Pt(II) precursor and N-donor ligand mediated by a base. Thus, the present investigation is believed to shed further insights concerning the dual role of coordinated OAc, as nucleophile and as internal base in C–H activation process mediated by platinum group metals.

2.3.5 CONCLUSION

Three classes of platinum(II) guanidine complexes of the types [Cl$_2$Pt(S(O)Me$_2$)L], [ClPt(S(O)Me$_2$)(C,N)] and [ClPt(OAc)(S(O)Me$_2$)L] were prepared in high yield and characterized by micro-analytical, IR and NMR ($^1$H, $^{13}$C, and $^{195}$Pt) data. Several new compounds including one novel acetate substitution product were characterized by single crystal X-ray diffraction data. The present investigation revealed the dual role of OAc$^-$ as a nucleophile and as an internal base in the C–H activation process of guanidines by platinum(II) precursor. The electronic/steric factors in conjunction with conformational features of of sym N,N′,N″-triarylguanidines appear to dictate the geometry of the platinum(II) atom in [Cl(X)Pt(S(O)Me$_2$)L] (X = Cl or OAc) and this in turn appear to decide the timescale of cycloplatination. The more preorganised cis,syn-anti geometry of [Cl$_2$Pt(S(O)Me$_2$)L] than any other geometries appear to be responsible for smooth C–H activation process. When both ortho positions of the aryl moieties of NHAr units are blocked as in XVIII, the C–H activation does not occur.
2.3.6 REFERENCES


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